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MARCH 1960
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TEXTILE RESEARCH JOURNAL

The Spinning of Rayon as Related to its Structure and Properties[1]

Wayne A. Sisson

Research & Development Division, American Viscose Corporation, Marcus Hook, Pa.

IN RECENT years, many new types of rayon have been introduced to the trade, each claiming to be an improvement or at least to have new properties which make the fiber better adapted for specific end uses. This paper is a general interpretation of how the rayon industry has improved the properties of rayon. This will be developed more from the physical-chemical point of view rather than from the engineering or fiber technologist's viewpoint, and I shall borrow freely from the literature and our own research without attempting to give due credit to the many people who have contributed to the concepts discussed.

General Theory

Basic Principles

By way of review, let us first consider some of the basic principles which determine fiber properties. These are:

1. Long chain molecules—their backbone structure, length, DP distribution, purity, flexibility, etc.
2. Functional side groups—their nature, distribution, polarity, size, etc. (cellulose = —OH).
3. Fine structure—arrangement of molecules
   a. Crystallinity—(lateral order)
   b. Orientation
4. Macro structure—fiber size, shape, surface, etc.
5. Aftertreatments—processing, finish, dyeing, resin treatments, etc.

I will not dwell upon Points 1 and 2 other than to quote an Englishman who recently described cellulose as a "jolly stiff molecule literally bristling with hydroxyl groups." Since cellulose is a product of nature, little has been done through the years to change the basic nature of this raw material used in rayon manufacturing. I must pay tribute, however, to the marvelous job which the pulp companies have done in improving the purity, DP distribution, and many other processing variables of wood pulp, without which improvements in rayon would not have been possible. The following is on the assumption that we have started with a good pulp.

Crystallinity

Since we no longer think of the cellulose in rayon existing as two discrete crystalline and amorphous phases, but rather as a structure which may vary between these two extremes, we prefer the term lateral order to designate an average or statistical state of affairs. However, I will still refer to crystal-

[1] Presented at the Gordon Research Conference on Textiles, July 8, 1958. The first half and the latter part dealing with tire yarn was presented at the Symposium on Rayon Tire Cord sponsored by the Dissolving Pulp Committee of TAPPI, February 23, 1959.

line and amorphous areas without implying that they are truly crystalline or amorphous.

Lateral order in rayon, for a given cellulose, is determined primarily by the degree of xanthation of the cellulose in the viscose and by the nature of the spinning bath. In other words, the lateral order is largely determined at the moment the filament is "born." If we extend the analogy to human beings, this might be termed the heredity factor.

Orientation

Orientation, on the other hand, is produced as the result of stretch after the filament is formed. Stretch may result from bath drag, friction over guides, by two driven godet wheels, or by tension during drying. This, by analogy, may be called an environmental factor. Just as humans are a product of their heredity and environment, so are the properties of a rayon filament a product of the structure born at the jet and to the subsequent environment.

Effect of Crystallinity and Orientation

In Table I are listed some of the effects of lateral order and orientation on three fiber properties: tensile strength, elongation, and reactivity (swelling, dye absorption, etc.).

If one wishes to obtain a complex property, such as toughness, which is proportional to the product of the two primary properties, strength and extensibility, then one must choose between two possibilities: a randomly oriented crystalline structure or a highly oriented amorphous structure. If we evaluate these effects quantitatively, we find that for high strength, high orientation is most important. Thus, we are left with the conclusion that if one wants to produce a tough rayon, then one would try to produce a fiber with the lowest possible lateral order (amorphous) and the highest orientation. For stiffness, which is proportional to strength divided by extensibility (slope of stress–strain curve), one should have high lateral order (crystalline) and high orientation.

Thus, by varying lateral order and orientation, one can obtain a wide range of physical properties in a rayon fiber.

Viscose

By way of review, let us next consider a typical viscose. The steps in preparing viscose are shown in Table II. The cellulose is (1) steeped in approximately 18% NaOH and the excess removed by pressing to obtain alkali cellulose. This alkali cellulose is aged, and then (2) xanthated or reacted with about 30–40% CS_2 (wt. of cellulose) to give sodium cellulose xanthate. This is then (3) mixed or dissolved in a 2–4% NaOH solution to form a high-viscosity viscose solution containing 6–8% cellu-

TABLE I. Effect of Lateral Order and Orientation on Fiber Properties

	Amorphous	Crystalline	Random	Oriented
Tensile strength	low	high	low	high
Elongation	high	low	high	low
Reactivity (swelling, dye absorption, etc.)	high	low	high	low

Toughness ∝ strength × elongation; stiffness ∝ strength/elongation.

TABLE II. Viscose Reactions

1. Steeping: $\text{Cell OH} + \text{NaOH} \longrightarrow \text{Cell—O—Na} + H_2O$
2. Xanthation: $\text{Cell ONa} + CS_2 \longrightarrow \text{Cell—O—C(=S)—S Na}$; $(\text{NaOH} + CS_2 \longrightarrow Na_2CS_3\ (H_2S, \text{etc.}))$
3. Mixing: $\text{Cell O—C(=S)—S Na} + \text{NaOH} \longrightarrow \text{Viscose solution}$
4. Ripening: $\text{Cell O—C(=S)—S Na} + H_2O \longrightarrow \text{Cell OH} + CS_2 + \text{NaOH}$
5. Spinning: $\text{Cell O—C(=S)—S Na} + H_2SO_4 \longrightarrow \text{Cell OH} + CS_2 + Na_2SO_4$

lose. During (4) a ripening period, while the viscose is deaerated and filtered, a slow splitting off of the xanthate groups takes place. As the xanthate groups split off, it becomes easier to coagulate the cellulose xanthate with an electrolyte such as NaCl. If we refer to a viscose having a salt test of six, this means that a 6% NaCl solution is needed to coagulate the viscose. At the proper salt test, the viscose is (5) spun into an acid bath which regenerates the cellulose.

Bath Components

Regeneration

One important reaction in the spinning process is the decomposition of cellulose xanthate to give cellulose. This is called regeneration and is favored by a low pH and by heat. Thus, hot H_2SO_4 is universally used to regenerate the cellulose and to neutralize the caustic in the viscose.

Coagulation

Coagulation, another important step, may be the complex result of several factors. For example, regeneration alone precipitates or coagulates the cellulose, but this is a comparatively slow reaction which must be aided by another mechanism: the salting out effect of a strong electrolyte, such as Na_2SO_4. Many other strong hydrating salts, such as $MgSO_4$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, etc., have a similar effect, but Na_2SO_4 is usually preferred because it is automatically formed by the reaction $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$. These salts also tend to buffer the H_2SO_4 and thus protect the filament from degradation by hydrolysis. The fewer the number of xanthate groups, the higher the DP, and the lower the NaOH, the easier it is to salt out the cellulose.

Compound Formation

$ZnSO_4$ also has a salting out effect, but it also performs another important function—that of insoluble compound formation. By an ion exchange mechanism, the unstable, soluble sodium cellulose xanthate is changed to a comparatively stable, insoluble, zinc cellulose xanthate. The Zn, being bivalent, also, where it has the opportunity, may produce a few cross links by reacting with the xanthates of two neighboring chains to form a cross-linked gel. The Zn xanthate reaction is very fast, and only small amounts are needed to coagulate a viscose as compared with the other mechanisms. Also, contrary to the salting out mechanism, Zn is more effective the greater the number of xanthate groups.

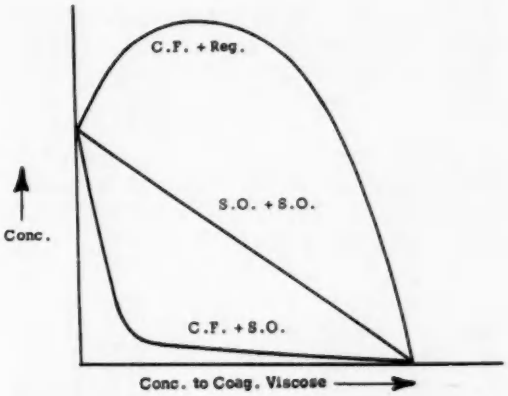

Fig. 1. Curves illustrating the combined effect of two spinning bath components when (middle line) both operate by a salting out mechanism (S.O.), when (bottom line) one operates by compound formation (C.F.) and the other by a salting out (S.O.) mechanism, and when (top line) one operates by compound formation (C.F.) and the other by regeneration (Reg.). For more detailed description of these curves see Horio, TEXTILE RESEARCH JOURNAL **20**, 373–381 (1950).

There are other metals, such as Fe, Co, Ni, Cr, Mn, Ag, etc., which have the same action as Zn. In general, most metals which form insoluble sulfides will work, but bivalent metals are preferred, Zn especially since it forms white or colorless compounds.

The above processes occur simultaneously, but at different rates. In some cases, chemical reaction rates predominate; in others, diffusion rates. The net result is a very complex situation. For example, the above coagulation effects may be additive, cooperative, or antagonistic, as illustrated in Figure 1.

In this figure, if the concentration of $MgSO_4$ necessary to coagulate a given viscose is plotted along the ordinate and the concentration of Na_2SO_4 on the abscissa, and then various mixtures of the two are plotted, the results are those anticipated—the middle straight line is obtained. Thus, for two compounds which coagulate by salting out mechanisms (S.O.), the combined effect is additive.

If, however, $ZnSO_4$ plotted along the ordinate and Na_2SO_4 along the abscissa are combined, the result is far greater than that anticipated from the coagulating power of the two components—the lower curve is obtained. In other words, the compound formation (C.F.) and the salting out (S.O.) mechanisms cooperate. The same is true of salting out and regeneration, but to a lower degree.

If we plot, on the other hand, $ZnSO_4$ along the ordinate and H_2SO_4 along the abscissa, we find they are antagonistic; the combined effect is less than anticipated—the upper curve is obtained. In other words, compound formation (C.F.) and regeneration (Reg.) mechanisms do not cooperate. This is reasonable, for if the acid splits off the xanthate groups, then the Zn can't cooperate by forming insoluble compounds.

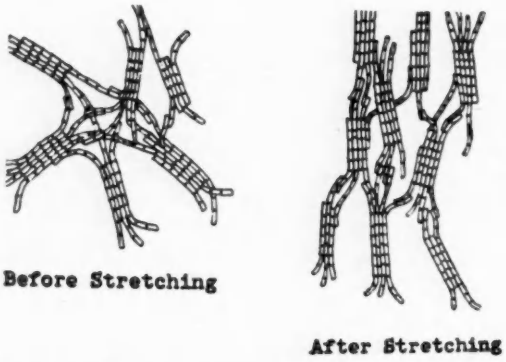

Fig. 2. Schematic representation illustrating the fine structure of a rayon filament before and after stretching.

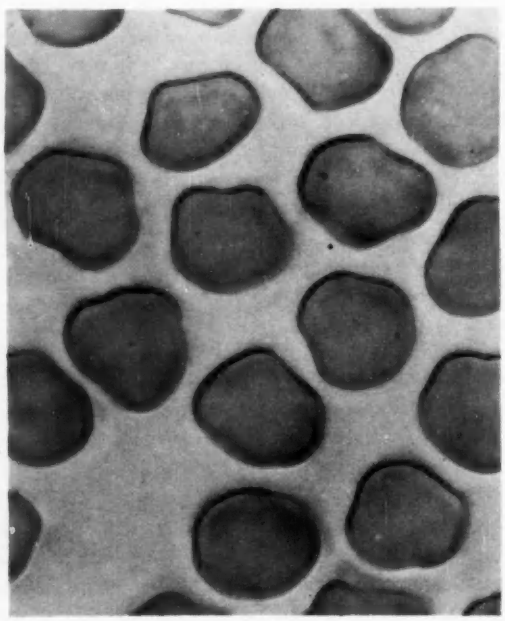

Fig. 3. Typical cross section of rayon spun in a bath where coagulation and regeneration are the principal mechanisms involved.

Dehydration

Dehydration or desolvation is another important mechanism in all spinning processes. A viscose solution usually contains 82–88% H_2O, which must be removed by osmosis. If one places a NaOH solution on one side of a cellulose membrane and, on the other side, a typical spinning bath, there is a rapid movement of the NaOH solution through the membrane to the bath side. If this were not true, it would be difficult to spin. The filament would set up as a weak swollen gel rather than as a strong compact filament suitable for processing on commercial equipment.

Typical Spinning Baths

Let us next consider three typical spinning baths (A, B, C) and how they affect the fine structure of the rayon. The various mechanisms involved and their sequence are

A. Coagulation, regeneration, and stretch.
B. Coagulation, stretch, and regeneration.
C. Coagulation and compound formation, stretch, and regeneration.

Coagulation, Regeneration, and Stretch

In this type of spinning, the procedure is to coagulate and regenerate the cellulose in the spinning bath and then stretch the regenerated cellulose. A typical bath would be H_2SO_4 and the Na_2SO_4. The coagulating mechanisms operating here are those of regeneration and salting out.

This gives a yarn with medium to high crystallinity, and the orientation would depend upon the stretch. The strength and extensibility are medium to low (e.g., 2 g./den. dry, 1.00 wet; 15% extensibility), high swelling (e.g., 90–100%), and a round, all-core cross section. Possible uses are carpet yarns and textiles.

Figure 2 is a schematic representation of the fine structure obtained with this type of spinning bath and the effect of stretching this type of structure. Crystal nuclei are formed at random and grow toward each other as far as the entangled chains will permit. Since the coagulation has proceeded ahead of the dehydration step, there is a tendency for chain aggregates or large crystalline areas to form, instead of a coherent structure with smaller crystalline areas. When stretch is applied, we get an alignment not of individual chains but of chain aggregates or crystallites connected by amorphous regions. One cannot

stretch this type of structure too much without disrupting or "tearing out by the roots," so to speak, the chains from their already established crystallites.

The final structure contains rather large crystalline and amorphous areas. The large disorganized amorphous areas give rise to large swelling, easy access to large dye and resin molecules, and a low wet stress–strain curve. The yarn is very sensitive to stresses during wetting and drying cycles. In other words, the yarn is very unstable, a condition which was typical of early textile rayons.

The cross section for this type of yarn, as illustrated in Figure 3, is in general rather round and smooth and has no skin.

Coagulation, Stretch, and Regeneration

Another method of spinning is to coagulate the cellulose xanthate in the bath, then stretch to orient the cellulose xanthate. Since the structure is stretched before it crystallizes, a higher stretch is possible; this gives better orientation. The oriented xanthate is then regenerated, which allows the cellulose to crystallize, forming more perfect, larger crystalline areas (higher lateral order). Note that this process differs from the previous one, where the cellulose was allowed to crystallize before stretching.

For this type of spinning, where the coagulating mechanism is principally that of salting out, such salts as $(NH_4)_2SO_4$, NaH_2PO_4, etc. or weak acids, like HOAc, may be used. These compounds are efficient buffers and as such can neutralize the NaOH in the viscose, yet operate at a pH high enough to avoid xanthate decomposition. Baths containing H_2SO_4 may also be used, provided sufficient buffering action is present to avoid excessive xanthate decomposition.

The above process gives a highly crystalline, highly oriented fiber. The fiber thus has a medium or high strength, low extensibility, high modulus, low swelling, and a round cross section. It is used where high strength, high modulus, and greater stability to moisture is desirable. The fiber, however, is brittle. It has a low fatigue; it may break down during many textile operations such as carding and may fibrillate upon repeated launderings, unless protected by further resin treatments.

Figure 4 illustrates a typical cross section of a yarn spun in a NaH_2PO_4 bath. Note that it is round, smooth, and has no skin.

Fibers with similar structure would be Fortisan, Lilienfeldt (Comptoir-B-X or Meryl), Fiber G, Z-54, etc. In Fortisan, the amorphous acetate is plasticized and highly stretched. The acetate groups are then saponified off to give a highly crystalline, highly oriented yarn. In the Lilienfeldt process, the viscose is spun in a strong H_2SO_4 bath, forming the sulfate ester, which is highly stretched and then saponified. Fibers such as Fiber G, Z-54, and other high wet modulus rayons now being evaluated by the trade are produced by stretching the xanthate derivative, followed by regeneration. All of the fibers discussed above have a common principle in that a derivative of cellulose is first stretched and then hydrolyzed, followed by crystallization, to produce a highly oriented crystalline fiber.

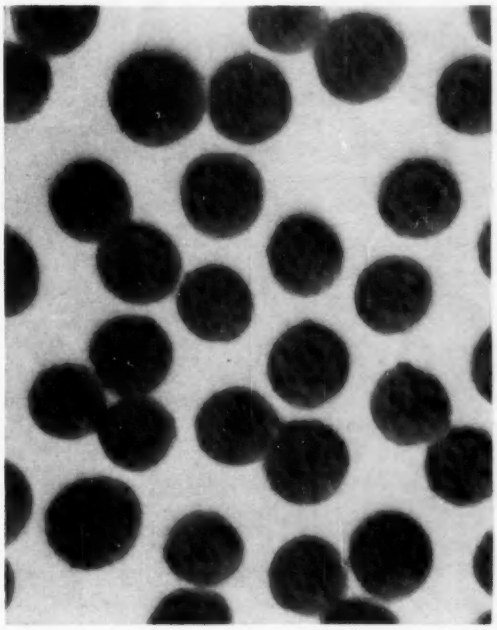

Fig. 4. Typical cross section of a rayon spun in a bath where coagulation is the principal mechanism involved. (C + H filter used to photograph core structure as black.)

Coagulation and Compound Formation, Stretch, and Regeneration

Next, let us consider a more complicated method of spinning where all three mechanisms of coagulation are involved. A typical bath would consist of H_2SO_4, Na_2SO_4, and $ZnSO_4$. Here the viscose is coagulated principally by Zn xanthate formation, aided by the salting out action of the Na_2SO_4, while at the same time some regeneration by the H_2SO_4 is taking place. Thus, the yarn, as it leaves the bath,

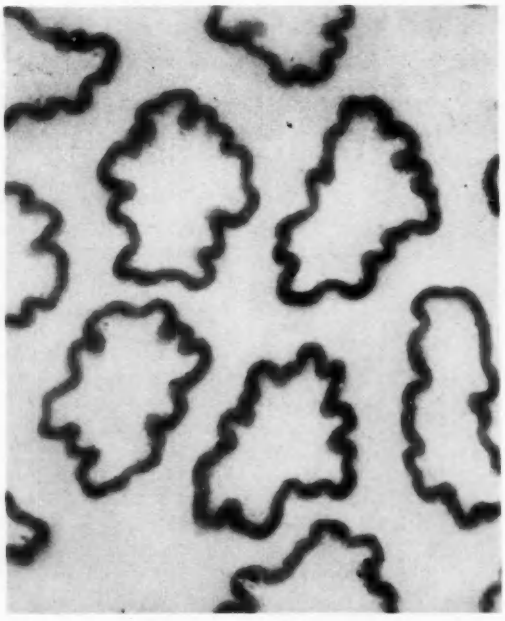

Fig. 5. Typical cross section of a rayon spun in a bath where coagulation, regeneration, and some compound formation take place.

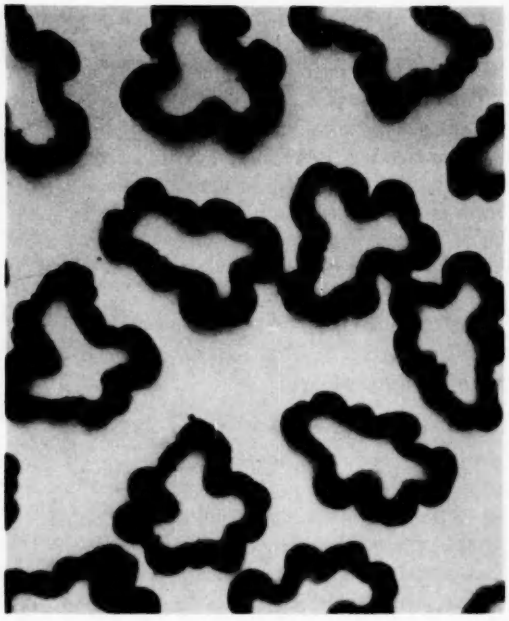

Fig. 6. Typical cross section of rayon produced by the same mechanisms as Figure 5, but with more compound formation (higher percent $ZnSO_4$ in spinning bath).

contains some Zn cellulose xanthate plus some regenerated cellulose. This is stretched, usually in a hot bath, and the Zn xanthate decomposed.

The resulting yarn has a low degree of crystallinity with small imperfect crystalline areas and usually a high orientation. This structure imparts to the fiber a high strength, high extensibility, lower modulus, and a serrated skin-core cross section. It is a tougher fiber than the other two types and is used in tire cord and industrial uses or wherever strength, fatigue, or abrasion is important.

Figures 5 and 6 illustrate typical cross sections when Zn is present in the bath. The yarn in Figure 5 contains a thin skin and is used in textile or apparel applications. It is produced by having present in the bath a small amount of Zn (for example, 1%). The yarn in Figure 6 has a thicker skin, and is designed for uses where greater strength and toughness is needed; it is produced by having a larger amount of $ZnSO_4$ (3–5%) in the bath. It is a typical tire yarn of several years ago.

The response of a thick and a thin skin yarn to godet stretch during spinning is shown in Figure 7. The tensile strength of the thick skin yarn increases slightly faster with godet stretch. The elongation for both yarns decreases, but most important is the fact that the curve for the thick skin yarn is on a higher level. Thus, we can increase the tensiles by increased godet stretch and still have sufficient extensibility left.

Effect of Zinc During Spinning

During spinning, zinc forms Zn cellulose xanthate, a fairly tough gel which is first formed on the outside of the filament while the interior is still liquid.

As the water is removed from the interior by osmosis, the cross section area is decreased and this outside skin has to adapt itself to a smaller diameter, which it does by puckering or folding on itself. The result is a serrated cross section. Thus, the shape of the cross section is determined largely by spinning conditions rather than by the shape of the spinnerette hole. The thickness of the skin is determined by how far the Zn penetrates into the filament before the xanthate groups are split off by the acid.

The Zn xanthate structure can be stretched more than a regenerated structure, and this makes possible a higher orientation.

It requires a greater force to stretch a Zn xanthate structure, and it is more elastic than a regenerated cellulose structure. This may be due to the cross-

linked Zn cellulose xanthate gel and to the fact that the Zn xanthate structure is less swollen than a regenerated cellulose structure.

With Zn spinning, more shrinkage takes place in the bath and less during drying. The amount of water in a filament as it leaves the bath is referred to as the gel swelling factor (weight of swollen fiber divided by weight of dry fiber). A filament formed in the presence of Zn may contain as low as 100% water (gel swelling = 2), while without Zn the water may be 300–400% (gel swelling = 4–5). We also have primary swelling—swelling of the washed but never dried filament—while secondary swelling is used to designate the swelling after the first drying.

The quick formation of Zn xanthate and the formation of a certain number of cross links while the cellulose chains are still in a disorganized state tend to initiate many crystal nuclei and thus prevent large crystal growth. In other words, Zn has a quenching action. Just as one prevents crystal growth while melt spinning a thermoplastic polymer, or casting a metal, by quickly passing through the temperature for optimum crystal growth, so does one prevent crystal growth in viscose by quickly passing through the optimum swelling range.

The final result is what we shall refer to as a skin type structure.

Identification of Skin

How do we identify a skin type structure? Figure 8 shows the cross section of a yarn shortly after being immersed in Victoria Blue dye. The core absorbs the dye at a more rapid rate than skin. If, after being fully dyed, the cross section is immersed in a deswelling agent, such as dioxane or alcohol, the structure shrinks. In this deswollen state, the dye can be leached out of the core but the dye molecules are trapped in the skin, as shown in Figure 9. In other words, the amorphous areas, or effective pore size of the skin, are critical for this particular dye. The dye can diffuse throughout a swollen skin structure but not a deswollen structure.

This type of photograph is what is usually seen in the literature. It is a photographic trick which makes the skin photograph dark and thus outlines the periphery of the fiber. It is misleading in that the skin actually dyes lighter. This skin dyeing technique works, regardless of whether the fiber is stretched or not. It is a lateral order effect and not an orientation effect. However, I should point out that there are other types of dyes which are more sensitive to orientation.

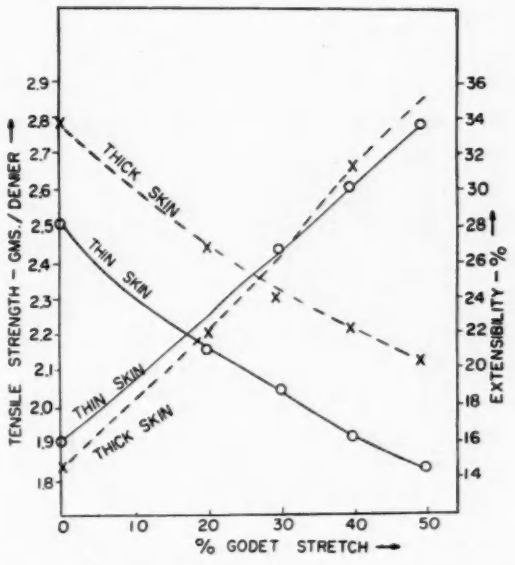

Fig. 7. Effect of godet stretch on the physical properties of a thick and a thin skin rayon.

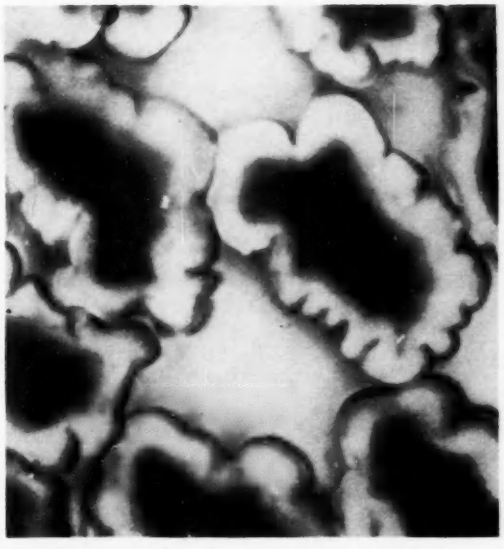

Fig. 8. Cross section of rayon filaments shortly after being immersed in the dye, Victoria Blue. For details see TEXTILE RESEARCH JOURNAL **15**, 444 (1945).

Electron Microscope Studies

We have attempted to study the skin and core structure in various ways. For example, we have cast thin, unoriented films with a skin and core structure and examined them under the electron microscope.

The surface replica of a core film magnified 100,000 times is shown in Figure 10; there is a hill and valley effect. If we assume the hills to be crystalline areas and the valleys to be amorphous areas which have shrunk during drying, we can estimate their size.

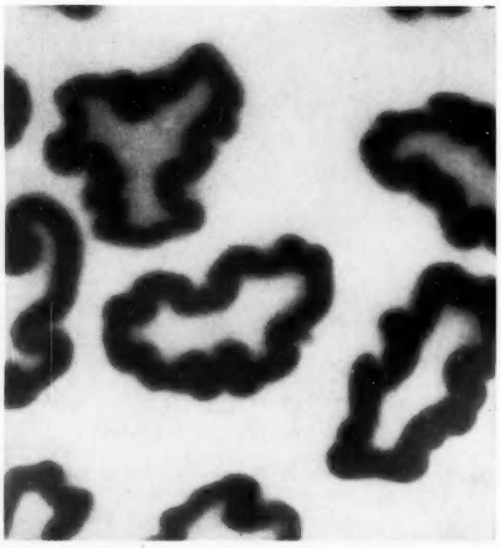

Fig. 9. Cross section of same sample as Figure 8 after being fully dyed, deswollen, and washed.

A skin film is shown in Figure 11; the hills and valleys are much smaller.

The measurements made on a skin and on a core film are shown in Table III. The crystalline areas in the core are about twice as large as those in the skin. In Table III are measurements made on two rayons, containing different amounts of skin, which had been hydrolyzed to their leveling-off DP and then broken down to small particles by ultrasonic vibration.

Average measurements on these particles and DP determinations show that the leveling-off DP of a skin structure is less than that of a core structure. X-ray diffraction studies also confirm the hypothesis that the skin is composed of smaller, less perfect crystalline areas.

Properties of Skin

A skin type structure can be identified by its behavior toward dyes. Its structure has a low lateral order with small crystalline and amorphous areas. Some of the properties of a skin structure as compared to that of a core structure are given below.

1. The swelling in water is less. For example, the core may swell 75–85% in cross section area as compared to 55–65% for the skin. One way of explaining this is that the cellulose chains are fixed in the crystalline areas at more frequent intervals; thus the

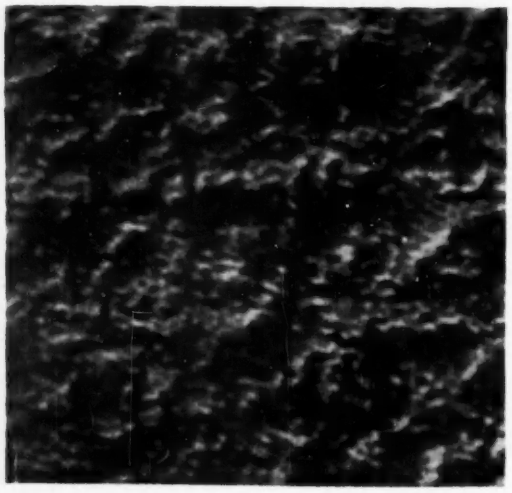

Fig. 10. Electron microscope surface replica photograph of a "core" structure.

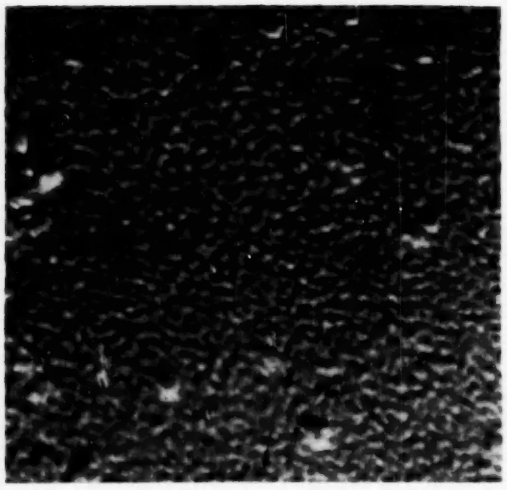

Fig. 11. Electron microscope surface replica photograph of a "skin" structure.

TABLE III. Length of Skin and Core Crystallites

Sample	Crystallite length, Å		
	Max.	Min.	Av.
Top or "skin" surface of film	150	70	104
Bottom or "core" surface of film	250	125	206
Tire yarn (60% skin, 40% core); measurements made on hydrolyzed yarn			145
Textile yarn (30% skin, 70% core); measurements made on hydrolyzed yarn			171

shorter amorphous regions or accessible portions of the chains have less opportunity to expand.

2. The moisture regain is higher. A rayon containing mostly core structure may have a moisture regain of 11–12%, while a thick or all skin rayon may have 13–14%. Offhand, one might expect the regain to be lower since the swelling is lower, but one must remember that the average lateral order is less, and this means that there are fewer OH groups bonded between neighboring chains to form truly crystalline areas. This leaves more OH groups available for bonding with water molecules, while swelling is limited by the network of smaller crystalline and amorphous areas.

Since hot stretching baths are often used in spinning thick skin yarns, there is frequently formed in rayon some cellulose IV, which is the high temperature equilibrium form for regenerated cellulose. However, we feel that whether the crystalline areas exist in the usual cellulose II or as cellulose IV is not as important as their size and perfection.

3. Owing to the smaller but more numerous amorphous regions of a skin structure, it can be just as accessible as a core structure to the diffusion of small, polar molecules like water. However, toward larger or less polar molecules, such as some types of dyes or resins, the skin structure may be less accessible. This must be taken into account when one tries to dye or resin-treat the various types of rayon. For example, a skin type structure may be less accessible to certain resins, yet very accessible to the H^+ used to catalyze the resin curing. The result is that the resin treatment is less effective while the loss in strength is greater because the cellulose chains in a skin structure are more accessible to the hydrolytic action of the H^+.

4. The density is less. This may be partly because the crystallinity or lateral order is less and partly because submicroscopic voids are usually present in the skin.

5. Because of these voids, a skin structure is usually more opaque and the refractive index lower.

6. Both the strength and the elongation of a skin structure are higher. This gives greater area under the stress-strain curve, and this means that it will absorb more work, is tougher, and has greater fatigue and abrasion resistance. In fact, it is impossible for a skin type structure to have a low elongation. A rayon with a permanent low elongation will usually have a low fatigue. This is why it is necessary to spin a high elongation yarn and then slash it down in order to obtain the 10% elongation desired by the tire companies. This low elongation, however, is not a permanent condition. The yarn will shrink back to a higher elongation when wet and dried relaxed. Also, the ratio of wet:dry strength is usually higher. In a core type structure, this ratio may be as low as 0.5, while in a skin type structure it may be as high as 0.8.

7. The modulus for a skin type structure is usually less for a given orientation. In recent years, the trend has been toward thicker skin rayons for textile applications. This, of course, has made them stronger and tougher, which our customers, the weavers and knitters, like, since it enables them to run their machines faster, but at the same time the yarns have become more limp and less crisp, and this has not been desirable for some textile end uses. Also, at the same time, they have become less amenable to finishing treatments designed to impart greater crispness and crease resistance.

8. The elastic recovery is usually better, especially wet. For example, when the yarn is elongated or slashed wet and then dried in the stretched condition, the recovery to the original length is much better when the yarn is again wet out and dried relaxed.

9. A highly oriented rayon has a tendency to fibrillate when subjected to abrasion or repeated launderings. This tendency is much less in a skin type structure owing to the action of the Zn during spinning in preventing the chains from becoming oriented and crystallized in parallel alignment.

Summary

By varying the viscose and spinning bath, it is possible to vary the lateral order and the shape of the cross section. By subjecting these structures, possessing different degrees of lateral order, to varying

degrees of stretch at the various stages of regeneration, it is possible to obtain a final structure with wide ranges in lateral order and orientation, the two basic fine structure factors which determine the properties of a rayon fiber.

Applications of Theory to Specific Products

Next, let us see how the principles have been applied in some rayon developments. I have selected crimped rayons, tire yarns, and carpet yarns for brief descriptions.

Crimped Rayons

A rayon spun by the route of a coagulated Zn xanthate (skin) structure is more elastic or more like a rubber band and is less swollen than a rayon spun by the route of regeneration and salting out. Also, a skin structure shrinks more during coagulation (lower gel swelling) while a core structure shrinks more during drying.

Films With Skin and Core

Figure 12 is a stained section of a wet film containing a skin and core, the core being the side next to the glass plate during casting. Note that the core side, owing to its greater swelling, takes the outside track of the bend.

Figure 13 is the same film after drying. Note that the core side, owing to its greater shrinkage upon drying, now has reversed its position and takes the inside track of the bend.

If we stretch this film, the effect of the greater elasticity of the skin side after stretching will predominate over the swelling effect and the skin side will occupy the inside track in both the wet and dry condition.

Thus, it follows that if one could spin a filament with more skin on one side, it would be a potentially crimpable yarn. This was first accomplished by spinning a so-called conjugate yarn.

Conjugate Filaments

The cross section drawing of a conjugate jet is shown in Figure 14. If two different viscoses are metered into the two inlets C and D and a septum B is located over the spinnerette hole A, the two viscose dopes are forced out of the spinnerette hole A side by side.

If the viscose entering C contains a large number of xanthate groups (high salt test) and Zn is in the bath, this half of the filament will be formed via the Zn cellulose xanthate route (i.e., skin structure).

If the viscose entering D contains few xanthate groups (low salt test), little stable Zn cellulose xanthate can form. The result is a cellulose structure

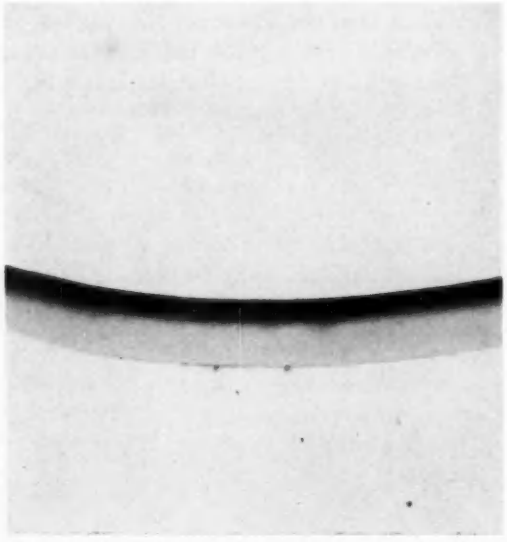

Fig. 12. Stained cross section of a wet film showing the effect of greater swelling of the core side upon direction of curling.

Fig. 13. Same film as Figure 12 after drying, showing the effect of greater shrinkage of core side upon reversing the direction of curling.

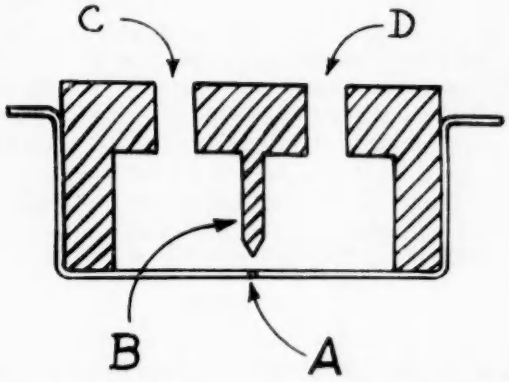

Fig. 14. Schematic cross section drawing of a conjugate jet.

produced by regeneration and salting out (i.e., core structure).

A cross section of the resulting conjugate filament is shown in Figure 15. Half of the filament contains a skin and the other half a thin skin or no skin. If this filament is stretched and then released, the skin half will have a greater contracting force.

The result is shown in Figure 16. The skin side, owing to its greater contracting force, has taken the inside track of a crimp bend. This is a spiral crimp, but here the fiber has been flattened between two glass slides for photographing.

Thus, if we have a filament possessing a bilateral structure with more skin on one side than on the other, the filament can be made to crimp either by stretching and relaxing or by swelling. Most commercial crimped rayons are produced by the stretching and relaxing principle. By this method, it is possible to produce as many as 40–50 crimps/in.

Chemically Crimped Filaments

In practice, an unbalanced skin–core structure is obtained without the use of special jets.

If a viscose containing a moderate number of xanthate groups is spun into a bath containing a small amount of Zn, a skin of Zn xanthate will be formed. If the regenerating acid is on the low side and the dehydrating Na_2SO_4 is on the high side, the shrinking force of the skin becomes so great that it splits, shrinks back upon itself, and exposes the interior of the freshly formed filament. The cross section of a yarn spun in this manner is shown in Figure 17. In effect, we have a little zipper on each filament which opens the skin and allows the interior to pop out. In practice, this ruptured position of a skin can be

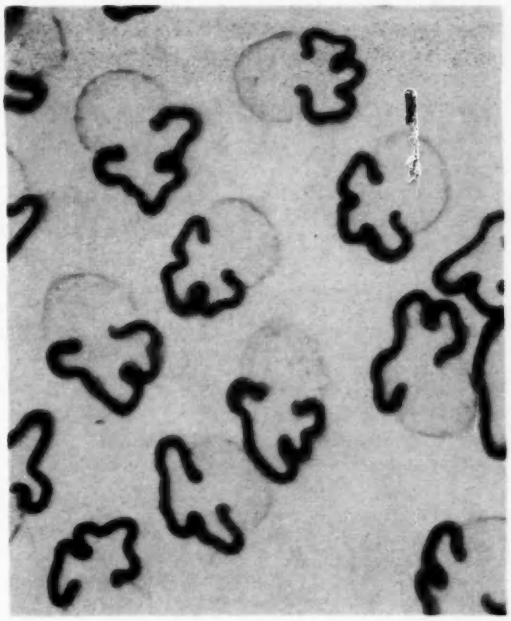

Fig. 15. Stained cross section of a conjugate filament spun from jet shown in Figure 14, showing skin structure on one side and absence of skin on other side of filament.

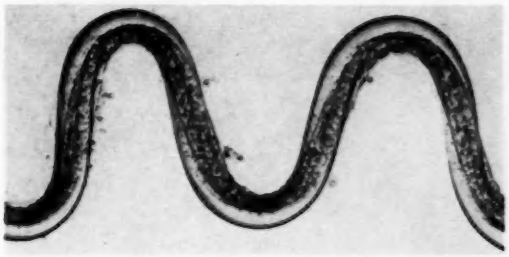

Fig. 16. Longitudinal view of filament shown in Figure 15, showing skin side taking the inside track of the crimp bend.

varied from large to small. In this way, the crimps per inch can be varied.

In some cases, especially with high Zn, an unbalanced cross section (more skin serrations on one side of filament) can be obtained without a clear-cut skin rupture. As illustrated in Figure 18, the cross section can be made unbalanced apparently by the flow of the bath striking one side of the filament or by the rupture taking place early. The crimps per inch here may not be as high but, with thicker skins, stronger yarns may be produced.

A potentially crimpable yarn, i.e., yarn supplied in a straight form but later crimped by the customer, can be made by the above processes. The customer produces the crimp by one of two methods: by immersing the fabric in a swelling agent, such as caustic, or by immersing it in water. In order for crimp to be activated by water, the yarn must be stretched or slashed and then dried under tension. Thus, upon wetting the yarn shrinks; since the skin structure shrinks more than the core, a crimp will be produced. This type of yarn can be used in such end uses as tufted rugs, where the rug is made with straight yarn and then crimped during the dyeing operation.

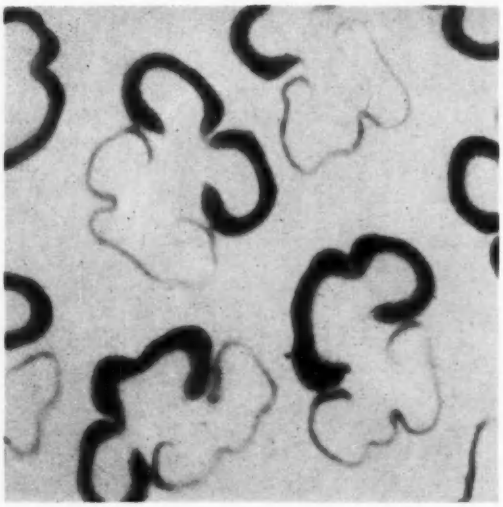

Fig. 17. Typical cross section of a crimped rayon filament, showing the ruptured skin. For further examples see TEXTILE RESEARCH JOURNAL **13**, 152–157 (1953).

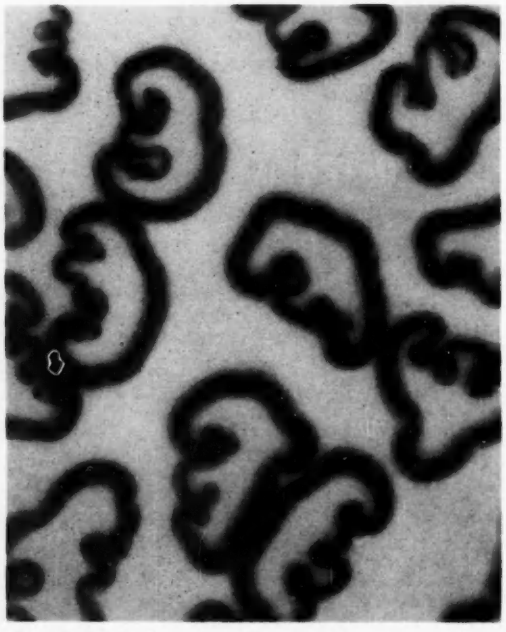

Fig. 18. Typical cross section of a crimped rayon filament which has unbalanced structure (more serrations on one side) without the presence of a ruptured skin.

Tire Yarns

During the 1940's, there was much research work done on the relationship between the fine structure of rayon and its physical properties. All of this work pointed to the conclusion that the best rayon tire cord would be one which contained the lowest

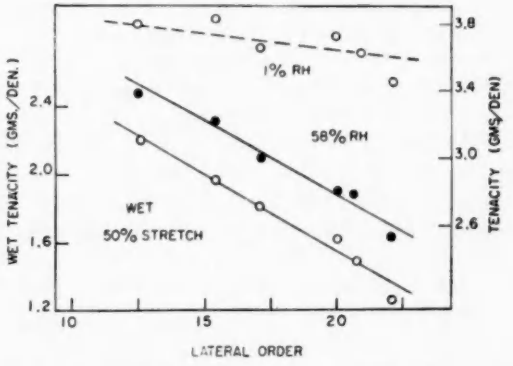

Fig. 19. Effect of lateral order at constant stretch upon the tenacity of rayon.

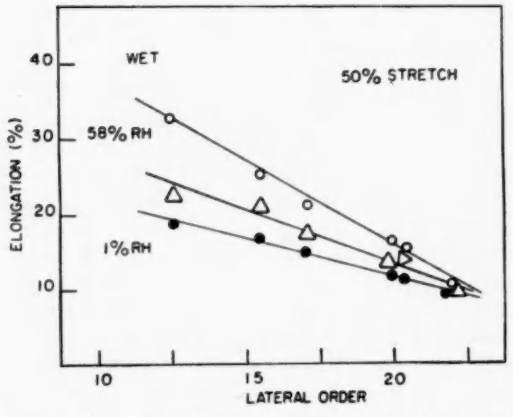

Fig. 20. Effect of lateral order at constant stretch upon the elongation of rayon.

lateral order and the highest orientation—the high orientation for strength and the low lateral order for fatigue.

Effect of Lateral Order

The unpublished results by Dr. Howsmon on a series of experimental rayons spun with the same degree of orientation but with varying degrees of lateral order are shown in Figure 19. The average stretch was only about 50% because the high lateral order samples could not be stretched more. As the lateral order decreases, the tensile strength increases, especially the wet and conditioned strengths. Also, there is a constant difference of about 1.2 g./den. between wet and conditioned strength; both approach the dry strength (1% RH) at low lateral orders.

Figure 20 shows the elongation plotted against the lateral order for the same yarns. Note that, for constant orientation, the elongation increases as the lateral order decreases. The wet and dry elongation approach each other at high lateral order but diverge quite widely at low lateral order, with the wet elongation increasing faster than the dry.

Figure 21 shows toughness versus lateral order for the same samples. Note that the 5% RH toughness, which is most important in tire yarns, is increasing slightly faster than the 58% RH toughness as the lateral order is decreased.

As this type of research work progressed, it became obvious that low lateral order is associated with a skin type structure. Furthermore, the practical observation was made that for a given strength level, the fatigue was better the greater the skin thickness.

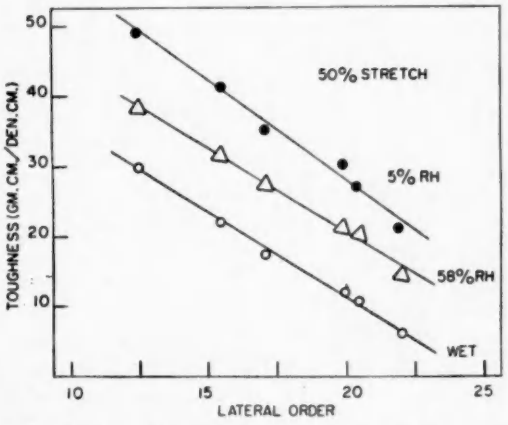

Fig. 21. Effect of lateral order at constant stretch upon the toughness of rayon.

Thus, in the middle 40's, we arrived at the conclusion that if one could spin an all skin yarn, the fatigue or toughness would be greatly increased.

How to Obtain Skin

How does one increase the skin thickness in a rayon? Some of the variables which contribute to skin formation are as follows.

In viscose, these variables are: the DP should be high with a narrow distribution; the ratio of caustic to cellulose should be high enough to obtain a good molecular solution; the number of xanthate groups per glucose unit should be high (high salt test)—this is most important; the byproduct sulfur should be high.

In the bath, a high Zn concentration is most important. The H_2SO_4 concentration should be low, or, to put it another way, the $NaOH:H_2SO_4$ ratio should be high to avoid rapid acid decomposition of the xanthate groups. The Na_2SO_4 concentration should be high to cooperate with the Zn and to give a strong salting out and dehydration effect.

When one tries to increase these variables, especially the salt test of the viscose and the Zn in the bath (the two most important variables), one runs into certain difficulties. For example, the point is soon reached where it is difficult to spin. Also, there are large amounts of gas formed which produce a

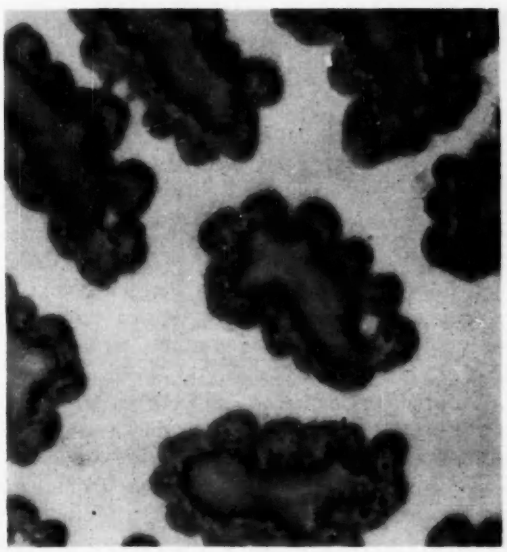

Fig. 22. Cross section of a rayon filament, showing the concentration of voids at the boundary between the skin and core.

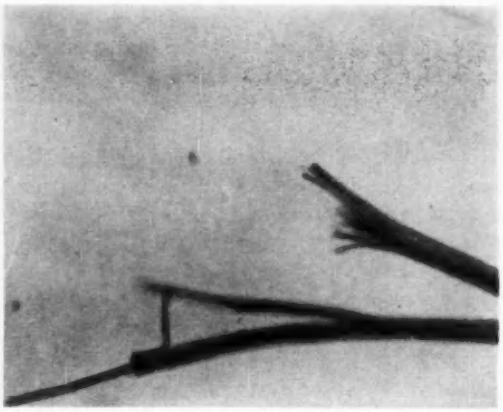

Fig. 23. Longitudinal view of a broken rayon filament, showing cleavage at the boundary between skin and core owing to concentration of voids at the boundary.

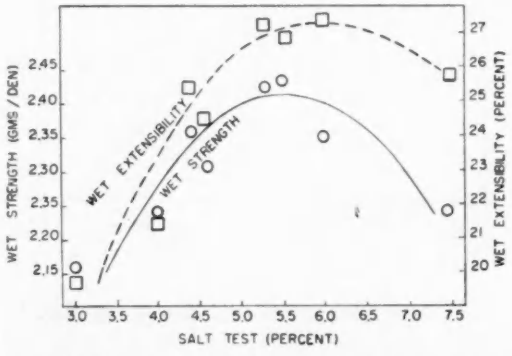

Fig. 24. Effect of salt test upon the wet strength and extensibility of a rayon tire yarn spun before the advent of super yarns (circa 1948).

porous structure in the yarn; this reduces the physical properties.

Some of the difficulties encountered with gas formation are illustrated in Figure 22. The voids tend to form at the boundary between the skin and core. In some cases, these voids may cause a rupture between the skin and core, as illustrated in the broken filament shown in Figure 23.

Also, the tensile strengths quickly reached a peak as one tried to increase the skin thickness by high salt test, as illustrated in Figure 24. In this specific case, the peak in wet properties is reached at a salt test between 5 and 6. This figure is from an old slide which I found in our files, but I think it represents the state of our knowledge in the middle and late 40's.

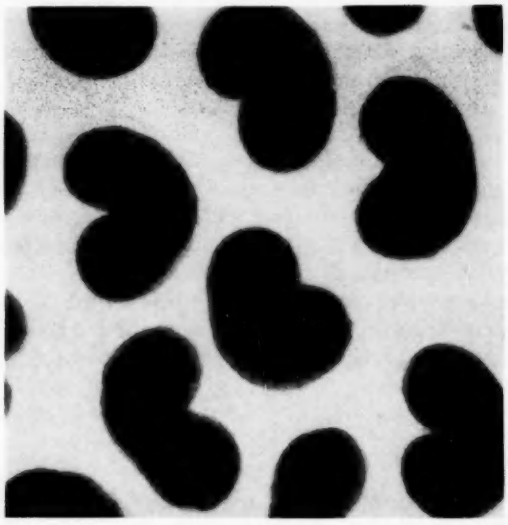

Fig. 25. Typical cross section of an all skin rayon spun from a high salt test viscose containing a modifier or additive.

In recent years, our knowledge of spinning has increased to the point where we can now displace this peak in tensile properties to a salt test of 12 or 13, or even 15. Furthermore, we now know how to obtain an all skin yarn, as illustrated in Figure 25. How was this accomplished?

All Skin Yarn

Definite progress in learning how to spin these all skin yarns began about 1950–1951. In 1950, it was disclosed in the Cox patents (U. S. 2,535,044; 2,535,045; 2,536,014) that, by adding small amounts of certain amines to the viscose, it is possible to greatly retard the regenerating process and thus enhance the Zn xanthate formation during spinning to the extent that one could produce an all skin yarn. In addition to an all skin cross section, the voids are very small and evenly distributed throughout the cross section.

Recently Dr. Smith [TEXTILE RESEARCH JOURNAL **29**, 32–40 (1959)] has shown the tensile strengths (dry, conditioned, and wet) of rayon tire yarns plotted against the year. These graphs show that the strengths have increased most rapidly since the advent of all skin rayons. This increase in tensile strength has been obtained without a decrease in elongation. In fact, the wet elongation has been increased at the same time; this is possible because of the decrease in lateral order.

This decrease in lateral order, along with an increase in orientation, has produced a marked improvement in fatigue, as illustrated in Figure 26, which is reproduced from Dr. Smith's paper. Along with improved fatigue has come increased retention of the single strengths when converted to cords.

Viscose Additives

In recent years, much work has been done toward searching for other chemicals which would produce an all skin tire yarn. There are now available many compounds; tire yarns made from viscose containing these compounds were known first as super tire yarns and more recently as super super or as super-2 yarns. Provided they meet other specifications of strength and fatigue, some of these yarns are advertised and sold under the name Tyrex.[2]

Types

These compounds, which make possible the production of all skin yarns, are known as viscose additives, viscose modifiers, or as regeneration retardants. In general, the types may be classified as amines, including mono-, di-, and polyamines and also quaternary ammonium compounds; ethylene oxide or propylene oxide polymers or copolymers; or ethylene oxide reacted with a wide variety of amines, alcohols, or acids. To this list also should be added the dithiocarbamates.

Effect

The effect of these additives is rather complicated, but the following should be mentioned.

The diffusion rate of H_2SO_4 into the filament or the NaOH out of the filament is retarded. This is easily demonstrated by putting an indicator into the viscose and noting the distance from the jet at which the color change appears. If an additive is placed in the viscose, and only 0.1% or less on the weight of the viscose is needed, the color change will double its distance from the jet. Or, if one casts a viscose film on a glass plate, it would take twice as long for the caustic to be neutralized in a viscose film containing an additive as it will for one without an additive.

The reaction rates are slowed down. For example, the xanthate decomposition or regeneration is retarded, as shown by analysis. Also, if one observes the distance from the jet at which gas is evolved, it will be noted that it is greatly increased.

More Zn xanthate is formed. By slowing up the acid diffusion, and thus protecting the xanthate groups from splitting off, the Zn is able to penetrate to the interior of the filament and react to form Zn xanthate throughout the cross section. This explains why we are able to obtain an all skin cross section.

The gel swelling is less. As previously pointed out, a Zn xanthate gel is less swollen or solvated than a regenerated cellulose gel. Thus, with a Zn xanthate structure formed throughout the cross section, a less swollen, tougher filament is formed. Furthermore, with Zn cellulose xanthate formed throughout the cross section, uniform shrinkage occurs; the result is a smooth, noncrenulated cross section. Its shape may be round, kidney-shaped, or flat. The ultimate, of course, when additive spinning conditions are pushed to their limit, is a round, all skin cross section.

Greater stretch is possible with a Zn xanthate structure.

The recent studies of Mithel, Saxton, Morgan, and Witkamp, [*Tappi* **42**, 559 (1959)] have given us new insight into some of the details of modifier action. They found that xanthate decomposition was only initially delayed by the presence of modifier and then speeded up, so that by the time hot stretch was applied, the gel-yarn had actually lower xanthate content than unmodified gel-yarn. On the other hand, the delaying influence of sodium trithiocarbonate on xanthate decomposition occurred only in the later stages of spin bath immersion.

Theory

A completely satisfactory theory, to my knowledge, has not as yet been advanced. Any theory must take into account the fact that many of the additives are effective when present in either the viscose or the bath, although they are usually more effective when

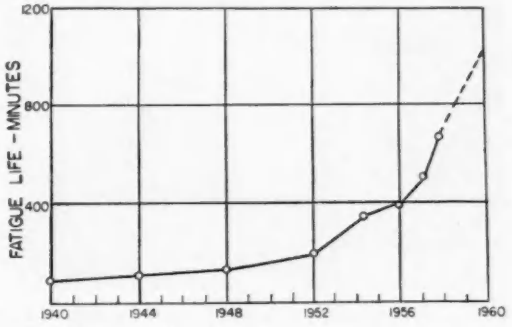

Fig. 26. Fatigue life of high strength rayon plotted against the year.

[2] Tyrex is a collective trademark of Tyrex Inc. for viscose tire yarn and cord.

used in the viscose. A theory also should explain why some types (amines) must be mixed with the viscose a considerable length of time before spinning in order to be effective, while others (ethylene oxide polymers) are effective immediately. Also, it must be remembered that these additives work only when Zn is present in the bath, when a large number of xanthate groups are present on the cellulose molecules, and when byproduct sulfur is present in the viscose.

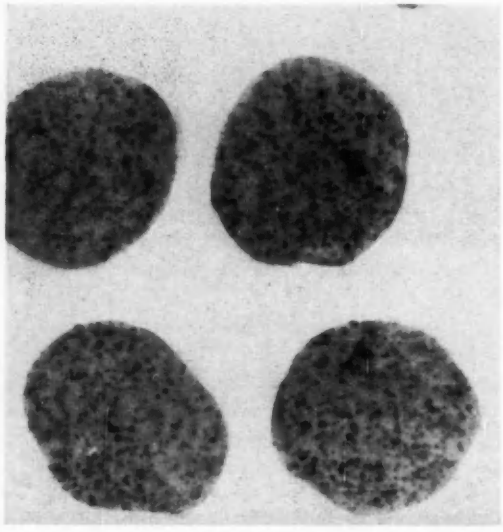

Fig. 27. Typical cross section of a delustered, all core type carpet yarn, showing a smooth surface.

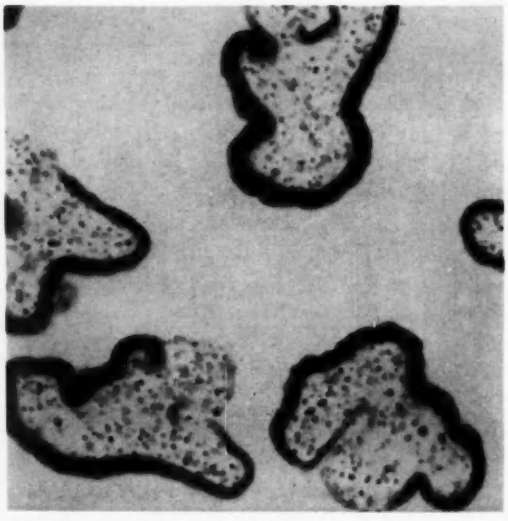

Fig. 28. Typical cross section of a delustered, crimped carpet yarn showing the presence of crenulations and the absence of skin on one side of the filament.

Several hypotheses, however, have been advanced which explain much of the observed behavior; I mention one for the amines which postulates the formation of a compound between Zn, the amine compound, and sodium trithiocarbonate, which is more soluble and thus can better penetrate to the interior of the filament. Another, but less plausible theory, is that an amine sodium dithiocarbamate is formed in the viscose which reacts with the Zn in the bath to form an insoluble Zn compound which acts as a barrier to the rapid migration of the acid into the filament.

One explanation for the polyethylene glycol or ethylene oxide derivatives is based upon the absorption of H^+ by each ether oxygen atom and that these absorbed H^+'s retard the migration of H^+ from the bath acid into the filament, yet allow the Zn^{++} to proceed.

These explanations, however, are oversimplified since not all amines or all ethylene oxide derivatives are effective. It does not seem possible to advance an explanation based on chemical reactions alone, since only a small amount of additive is nee ed to produce a pronounced effect.

It seems to me that the most logical theory would be the formation of some sort of a semipermeable membrane or molecular layer which retards the migration of the H^+ into the filament yet does not re-

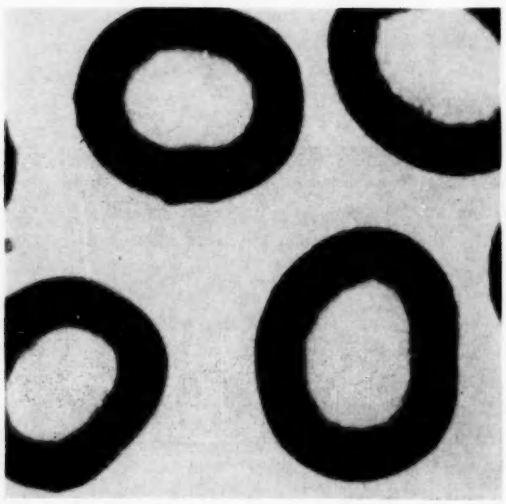

Fig. 29. Cross section of an experimental carpet yarn, showing the presence of a skin and a smooth surface.

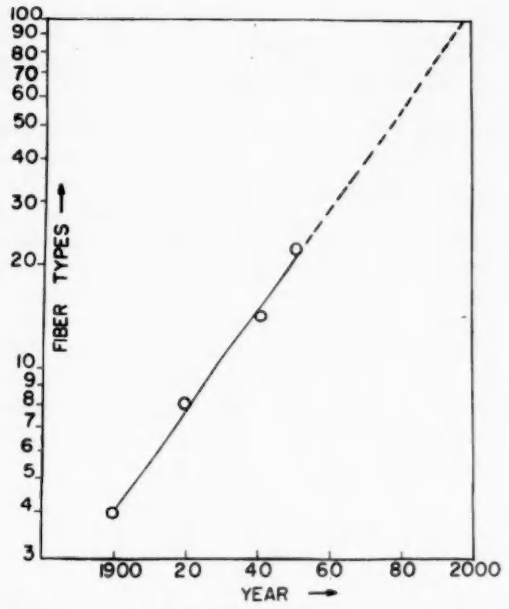

Fig. 30. Graph plotted on a semilog scale, showing the relationship of the total number of major types of fibers introduced to the trade plotted against the year.

tard the migration of the Zn into the filament or the OH^- out of the filaments.

Effect of Yarn Structure

There are different types of skin. Before additive spinning, the research man could anticipate the toughness of an experimental yarn by observing the skin thickness. Now, with all skin yarns, there is no simple technique like staining to screen the progress being made. One has to resort to other more complicated techniques, such as x-ray diffraction, for estimating the lateral order and the orientation, which are the most important parameters for further identifying the type of skin.

In an all skin yarn, the voids are absent or very small and evenly distributed throughout the cross section. It has been theorized that the presence of small voids enhances the fatigue of tire yarns by allowing them to absorb energy through collapse of the voids rather than through molecular flow.

Effect on Yarn Properties

In general, yarn properties are those predicted for a skin structure. However, the presence of all skin, as indicated by a staining technique, does not guarantee superior strength and fatigue. A skin type structure is desirable, but alone is not a sufficient condition for producing a tough yarn—in addition, the orientation must be high and the lateral order low.

Problems

If this technical information has been available for several years, one may ask why greater progress has not been made in the production of rayon tire yarns with greater strength and fatigue. As with any new development, new problems have arisen.

Super spinning has required a new technical know-how. This has been very frustrating to production people and management who have come up through production when they find that their long years of experience no longer apply. This makes it difficult to transfer research information into production.

Additive spinning requires slower speeds, and this is adverse to our modern age of speed, especially to the economics of production.

Zn xanthate is difficult to decompose, and most continuous spinning machines are not designed for this extra step.

Many good additives are also good detergents, thus produce foaming problems and homogenize air into the viscose which is difficult to remove.

The detergency action of many additives also peptize dirt particles and make them difficult to filter out.

However, in spite of these and many other difficulties, progress is being made and, I think, will continue to be made in the tire yarns. Also, the technology developed in tire yarn spinning is being adapted to rayon staple production, and further improvements in this area can be expected.

Carpet Yarns

Some of the properties desired in a carpet yarn are resilience, long wear (abrasion resistance), lack of soiling, and good cover.

Increasing the stiffness is the only way we know to increase the resilience in a rayon fiber. Thus, resilience (or stiffness) could be peaked by increasing crystallinity and orientation, but this small gain in resilience would be obtained at the cost of a large loss in abrasion or toughness. Abrasion (or wear life) could be improved by decreasing both the orientation and the crystallinity, but since crystallinity is decreased by adding Zn to the bath, this introduces crenulations in the cross section which would increase the soiling. Good cover could be obtained with crimp,

but since Zn in the bath and stretch are needed to produce crimp, this increase in orientation would mean a reduction in wear and the crenulations from the Zn an increase in soiling. Thus, as in many textile problems, a compromise must be made.

The cross section of one type of carpet yarn is shown in Figure 27. It has been spun without Zn in the bath to obtain an all core, round cross section with a comparatively smooth surface to minimize soiling. Abrasion is improved by low orientation, which gives high extensibility. Thus, abrasion and soiling are peaked at the expense of resilience and cover. This is done because resilience in cellulose is inherently rather poor and cannot be improved without introducing excess brittleness (low abrasion). Cover can be improved by fabric construction features, such as twist, bulking, etc.

In Figure 28 is the cross section of a crimped carpet yarn which would give cover to the carpet, but the soiling and abrasion resistance would not be as good as the yarn in Figure 27.

The cross section of an experimental thick skinned smooth surfaced yarn is shown in Figure 29. It should give longer wear and lower soil retention. However, the cover is poor, and the skin structure gives a limp yarn which tends to lie down rather than stand erect in the pile.

Summary

We have seen that it is possible to produce such widely varying structures as all core, skin-core, broken skin, and all skin rayons. These, combined with varying degrees of orientation, make possible a wide variety of properties.

Future Growth of Fibers

Several years ago (1951), I showed Figure 30 at one of our sales meetings. Here we have the total number of major types of fibers which have been introduced to the trade plotted on a log scale against the year. For example, in 1900, we had four major types of fibers—cotton, wool, silk, and linen. By 1920, we added viscose rayon, nitrate, cuprammonium, and acetate—a total of eight—and so on up to 1951 when this was plotted. I have not brought the curve up to date, but my guess is that the new fibers are appearing at the predicted rate, and it is interesting to note that the extrapolated curve predicts over 100 different fibers by the turn of the century.

I have not plotted a similar curve for the various varieties of rayon which have appeared on the market, but I feel fairly sure that a similar type of curve would be obtained, or at least I expect it for the future. For when one adds to the fine structure variables discussed in this paper the variables of denier per filament, cross section shape, delustrants, spun-in pigments, inflated yarns, thick and thin yarns, resin treated yarns, etc., the possibility of producing a variety of yarns for specific end uses becomes large indeed, and I think many of them will be produced. In fact, the future of rayon appears to be toward the production of many new types of rayon, each engineered to meet the requirements of specific end uses.

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New Silicone Alloy for Durable Water Repellency on Cotton[1]

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Abstract

A new silicone alloy made by the simultaneous polymerization of tetravinyl silane and methyl hydrogen siloxane using benzoyl peroxide as a catalyst and methyl isobutyl ketone as a solvent is an excellent water repellent for cotton fabrics as measured by AATCC spray ratings. The treatment is very resistant to soap and detergent action. The alloy may be applied from organic solvents or aqueous emulsions. Greater permanence to laundering was obtained by the solvent method. Best results were obtained by first depositing ZrO_2 in the fabric by double decomposition using a zirconium salt and sodium hydroxide, then padding with either a methyl isobutyl ketone solution or an aqueous emulsion of the alloy and curing for 5 min. at 145° C. A satisfactory one-step process was also developed by incorporating zirconyl acetate or zirconium butoxide as catalysts in the treating solution or emulsion. Creaseproofing resins may also be incorporated in the formulation.

THE TEXTILE industry has long been familiar with the use of silicones to impart softness of hand and water repellency to synthetic fibers. More recently silicones have been developed for use on cotton [7]. Usually encountered in this field are the dimethyl silicones and methyl hydrogen silicones [8]. These two silicones are usually combined in treating cotton for water repellency, the dimethyl silicone giving softness and the methyl hydrogen silicone giving permanence. However, the usual disadvantage in the silicone finishes lies in only a moderate degree of durability to laundering.

The chemical structure of tetravinyl silane suggested the possibility of water repellency in applying the silane alone to cloth, or by the addition of hydrogen siloxanes across the vinyl double bonds and applying this silicone to cloth. Appearance of tetravinyl silane on the market in pilot plant quantities provided a source of this material for experimentation. There are few references to tetravinyl silane in the literature. The synthesis of this compound was carried out in Russia by the Wurtz reaction [10], using silicon tetrachloride and vinyl chloride in the presence of sodium. Brief mention is made in a British patent in connection with its copolymerization with styrene, methyl methacrylate, and vinyl acetate to give cross-linked polymers for use in coating and impregnating [6].

The present paper describes the development, and application to cotton, of a new silicone alloy from tetravinyl silane and methyl hydrogen siloxane. (Note: an alloy is a composite material made up by blending polymers or copolymers with other polymers or elastomers under selected conditions [9].)

Materials and Methods

The cotton materials used in most of the evaluations were bleached 80 × 80 print cloth weighing 3.1 oz./sq. yd. and desized, scoured, bleached, and mercerized 140 × 64 broadcloth (3 oz.). Several other types of cotton fabrics and modified cotton fabrics were evaluated briefly, along with some synthetic textile materials.

Chemicals

The tetravinyl silane (TVS) used was a clear, low boiling liquid which is available in pilot plant quantities from Metal and Thermit Corporation.[3] The

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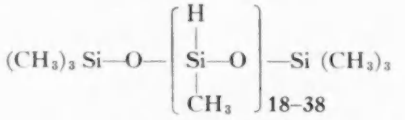
[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] Throughout this paper, the mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

methyl hydrogen siloxane (MHS) was a commercially available siloxane, having the formula



Methyl isobutyl ketone (MIBK), a commercial grade of ketone, was used as the principal polymerization medium for the TVS and MHS. Benzoyl peroxide was the polymerization catalyst for TVS and MHS. A number of zirconium compounds were used as catalysts in the application of the TVS-MHS polymers to fabrics; they are described below in the appropriate places.

Processing Procedures

The polymerization of TVS and MHS was carried out in a three-neck, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The concentrated polymer solutions were kept in a refrigerator to minimize any further polymerization. The concentrates were diluted as needed. Two methods of application to fabrics were used: solvent method and aqueous emulsion. The emulsion was prepared by mixing in a Waring Blendor. The fabric samples were padded using a laboratory padder and cured in a forced draft oven. The samples were then process washed, dried, and evaluated. The process wash consisted of 3 min. in warm running tap water.

Test Methods

The following properties were measured by the usual ASTM procedures: tearing strength, Elmendorf method [2a]; breaking strength, strip method [2b]; crease recovery, Monsanto method [2c]; and flex abrasion [2d]. Water repellency was rated by the AATCC Standard Spray tester [1] under prevailing room conditions. The soap-soda boil consisted of boiling for 1 hr. in water containing 0.5% soap chips and 0.2% sodium carbonate. The detergent boil consisted of boiling for 1 hr. in water containing 0.5% Tide. Laundering was carried out in a home-type tumbler machine, using Tide as the detergent; tumble drying was done also in a conventional home-type dryer.

Results and Discussion

Polymerization of Tetravinyl Silane (TVS)

Six grams of tetravinyl silane (TVS) and 0.06 g. (1.0% based on TVS) of benzoyl peroxide were dissolved in 4.0 g. of methyl isobutyl ketone (MIBK). The solution was heated with stirring for 90 min. at 80° C. The resulting solution was diluted to 200 ml. with MIBK to make a 3% polymer solution by volume.

The 3.0% solution of TVS polymer was padded onto a sample of broadcloth and cured at 145° C. for 5 min., process washed, and dried. The fabric had a stiff hand and a spray rating of about 50. The water repellency was reduced to zero by rubbing the fabric between the fingers.

The polymerization of TVS was carried out at several other catalyst concentrations (0.1–4.0%) with similar results.

A solid polymer could be isolated from the MIBK solution by the addition of dimethyl formamide.

Polymerization of Methyl Hydrogen Siloxane (MHS)

Polymerization of MHS was carried out exactly in the same manner as that used for TVS. The polymer was also applied to untreated broadcloth in the same manner as used above. The fabric had a soft hand and a spray rating of 80. The spray rating was reduced to 50 by boiling for 1 hr. in a soap and soda solution. Higher spray ratings of a more durable nature were obtained when poly MHS was applied to resin treated cloth.

The polymerization of MHS was carried out at several other catalyst concentrations (0.1–4.0%) but the results were about the same as above. During the polymerization of MHS there was an increase in viscosity. If the polymerization was allowed to proceed far enough, a waxy solid could be obtained. The reason for this is not fully known but is probably oxidation, since hydrogen is released.

Simultaneous Polymerization of TVS and MHS

Preliminary experiments indicated that a useful water repellent might be made by polymerizing TVS and MHS simultaneously in a suitable organic solvent. In order to establish preferred procedures, experiments were carried out in which time, temperature, catalyst concentration, and ratio of TVS:MHS were varied. Both methyl isobutyl ketone (MIBK) and xylene were tried as solvents. In all experiments the weight ratio of solvent to reactants was 2:3. Both solvents were found to be satisfactory media for polymerization. However, the xylene method required a much longer period of time than the MIBK method; up to 24 hr. at 120° C. was required. The polymerization catalyst employed was benzoyl per-

oxide. Catalyst concentrations of 0.1–1.0% were tried; the latter concentration was found to be the most satisfactory. A typical procedure for the more satisfactory MIBK method is given below.

Twelve grams of TVS, 60.0 g. of MHS, and 0.72 g. of benzoyl peroxide were dissolved in 48 g. of MIBK. The solution was heated with stirring for 90 min. at 80° C. The resulting solution showed a distinct colloidal haze. The polymer solution was diluted to the desired concentration with MIBK before application to cotton fabric.

A 3% solution (weight per unit volume) of the above TVS-MHS polymer was padded onto broadcloth and cured at 145° C. for 5 min. The fabric was white and had a nice soft hand. It had an initial spray rating of 100, and a spray rating of 70 after boiling for 1 hr. in a soap and soda solution. The TVS-MHS polymer treatment showed considerable improvement over the separate treatments in imparting permanent water repellency to cotton fabrics.

It seemed very likely that methyl hydrogen silicone could add to the double bonds of the tetravinyl silane to produce a copolymer. Therefore, attempts were made to demonstrate that a copolymer was produced, but more evidence was found to indicate that the two components merely polymerized simultaneously to form an alloy. This was most strongly indicated when identical water repellency and durability results were obtained either by carrying out the polymerization with both TVS and MHS in the system or by separately polymerizing the two compounds and then combining the polymer solutions before application to fabric.

Time and Temperature Study on Polymerization of TVS and MHS

Preliminary experiments were carried out in which TVS and MHS (1:1 weight ratio) were polymerized at temperatures ranging from 70–120° C. and times of 30–240 min. Benzoyl peroxide, 1% based on the weight of TVS and MHS, was used as a catalyst. The various polymers were diluted with MIBK, applied to small swatches of fabric, and the appearance and water repellency examined. By this procedure, a temperature of 80° C. and reaction times of 60–120 min. were selected as the best conditions for further study. The spray ratings of fabric dropped off sharply if treated with polymers prepared at 80° C. for 150 min. or longer, or with polymers prepared in 30 min. or less at 80° C.

Study of Ratio of TVS:MHS

A series of polymerizations was carried out in which the ratio of TVS:MHS was varied from 1:1 to 1:10. Another polymerization was carried out in which the ratio of TVS:MHS was 5:1. Finally, two additional polymerizations were carried out to serve as the extremes. In one of these reactions the MHS was omitted, and in the other the TVS was omitted. All of the reactions in this series were carried out at 80° C. for 90 min. or 120 min., using 1.0% benzoyl peroxide as a catalyst for the alloy preparation and MIBK as the solvent. Each of the polymers was diluted to 1% or 3% concentration with additional ketone and cured on 80 × 80 print cloth or broadcloth at 145° C. for 5 min. or 160° C. for 10 min. The spray ratings before and after a 1-hr. soap-soda boil are given in Table I for broadcloth samples treated with 3% solutions of the polymers. The best spray ratings were obtained on the samples treated with mixtures of the TVS and MHS. These samples, with one exception, had initial spray ratings as high as 100 and ratings of 70–80 after a 1-hr. soap-soda boil. The samples cured at the higher temperature of 160° C. generally had higher spray ratings after the soap-soda boil than those cured at 145° C. All of the fabrics treated with the alloys had a soft hand except the ones treated with the TVS:MHS ratio of 5:1 and the ones treated with poly TVS. These had a slightly stiff hand. It was concluded from this series of experiments that a good alloy composition was the TVS to MHS ratio of 1:5. In general, the spray ratings of treated 80 × 80 print cloth were slightly lower than those of broadcloth.

Metal Oxide Catalysts for Alloy

It is well known that catalysts are necessary for obtaining the best results when applying silicones to fiber surfaces. Several metal compounds have been used as catalysts, such as fatty-acid salts of zinc, lead, and tin, as well as alkyl esters of orthozirconic and orthotitanic acids [8].

In previous experimental work at this Laboratory, it was discovered that considerable water repellency was imparted to cotton fabric by treatment with a ferric hydrosol in which the beta ferric oxide was deposited on the fibers. It was found that when a MIBK solution of the TVS-MHS alloy was applied to fabric coated with beta ferric oxide, much better water repellency was obtained than with either the polymer or the oxide alone.

TABLE I. The Influence of Weight Ratio of TVS to MHS On Water Repellency of Broadcloth

Weight ratio of TVS to MHS*	Curing time, min.	Curing temp., ° C.	Initial spray rating	Spray rating after soap-soda boil
0/1	5	145	80	50
1/0	5	145	50	<50
1/1	5	145	90	<50
1/5	5	145	100	70
1/10	5	145	100	70
5/1	5	145	80	<50
0/1	10	160	90	<50
1/0	10	160	50	<50
1/1	10	160	100	70
1/5	10	160	100	80
1/10	10	160	100	70
5/1	10	160	100	70

* The polymers with a 1/1 ratio of TVS to MHS were prepared by heating at 80° C. for 120 min. All the others were prepared at 80° C. for 90 min.

TABLE II. The Influence of Metal Oxide Catalysts on Water Repellency

Metal oxide*	Type fabric	Initial spray rating	Spray rating after soap-soda boil
Fe_2O_3	Print cloth	100	<90
Fe_2O_3	Broadcloth	100	90
ZnO	Print cloth	100	70
ZnO	Broadcloth	100	70
CeO_2	Print cloth	100	70
CeO_2	Broadcloth	100	70
TiO_2	Print cloth	100	80
TiO_2	Broadcloth	100	90
ZrO_2	Print cloth	100	90
ZrO_2	Broadcloth	100	100

* Each fabric sample had a metal oxide add-on of about 0.5%.

TABLE III. The Influence of ZrO_2 Concentration on Water Repellency

ZrO_2 add-on to fabric, %	Initial spray rating	Spray rating after soap-soda boil
0.0	100	70
0.1	> 90	>80
0.2	100	90
0.4	100	90–100
0.8	100	90–100
1.5	100	90

Since ferric oxide imparted a yellow color to the fabric, several other metal oxides were investigated as catalysts. These included ZnO, ZrO_2, CeO_2, and TiO_2. All of these oxides were deposited on the fabric by first padding through a solution of the metal acetate, chloride, or sulfate and then through a solution of sodium hydroxide, followed by washing and drying in an oven. Then a 3% solution of the TVS-MHS alloy (1:1 weight ratio, polymerized at 80° C. for 90 min.) was padded onto oxide-treated samples of print cloth and broadcloth and cured for 5 min. at 145° C. It has been previously stated that a curing temperature of 160° C. for 10 min. was necessary to get a water-repellent finish which was reasonably stable to an alkaline boil when the water repellent was applied without a metal oxide catalyst. It was found that the curing time and temperature could be reduced to 5 min. at 145° C. when employing the metal oxide catalysts and better water repellency could also be obtained. The spray ratings of the various catalyzed fabrics are shown in Table II. Best results were obtained with Fe_2O_3, TiO_2, and ZrO_2. The spray ratings of these three were 90–100 after a 1-hr. soap-soda boil. Initial ratings of 100 were obtained with all of the catalysts. Spray ratings of 80 were obtained on Fe_2O_3 and ZrO_2 treated broadcloth after a 1-hr. soap boil, even when treated with a 1.0% solution of TVS-MHS. Ceric oxide and ferric oxide had the disadvantage of being yellow. The TiO_2 treatment degraded the fabric somewhat since it was applied to the fabric initially from a hydrochloric acid solution of $TiCl_4$. Therefore, ZrO_2 seemed to be the best catalyst for further study. Fabrics treated with ZrO_2 were white and, like all the other samples in Table II, had a soft hand.

Study of ZrO_2 Concentration

Samples of broadcloth were treated with zirconyl sulfate and sodium hydroxide to give add-ons of ZrO_2 varying from 0.1% to 1.5%. The samples were then padded through a 3% xylene solution of TVS-MHS polymer (weight ratio of 1:2, polymerized in xylene at 120° C. for 24 hr.) and cured at 145° C.

TABLE IV. Effect of Aqueous Emulsions of the Alloy on Broadcloth

Type treatment	Initial spray rating	Spray rating after soap-soda boil	Spray rating after detergent boil*
Alloy alone	100	> 80	90
Alloy + 0.5% ZrO_2	100	100	<100
Alloy + 0.5% Fe_2O_3	100	<100	<100
Alloy + 5.0% triazone	100	80	< 80
Alloy + 5.0% triazone + 0.5% ZrO_2	100	100	100

* These spray ratings were on samples given the soap-soda boil followed by an additional detergent boil.

for 5 min. The spray ratings before and after a 1-hr. soap-soda boil are shown in Table III.

The best catalyst add-on was 0.4–0.8%, as shown by spray ratings of 90–100 after a 1-hr. soap-soda boil.

Aqueous Emulsion of the TVS-MHS Alloy

With the idea of developing a more practical procedure for the application of the polymer blend to cotton, several aqueous emulsions were prepared using a variety of emulsifying agents. Ethomid 0/15 (ethoxylated oleamide, produced by Armour Chemical Division) was found to be the most satisfactory emulsifying agent of the ones tried. Two methods of emulsification were tried. In one a concentrated MIBK solution of the alloy (as obtained in the polymerization procedure) was used. In the other, the MIBK was removed under vacuum, and the 100% polymer emulsified. The former method gave the best results, presumably due to the presence of MIBK. In the latter method the 100% polymer continued to polymerize slowly on storage with the separation of solid polymer. Better results were obtained by the latter method if MIBK were added to the aqueous emulsion. A typical procedure for the preparation of an aqueous emulsion is given below.

Ethomid 0/15 (0.22 g.) was dissolved in 9.4 g. of polymer solution (60% alloy, 40% MIBK) and added to 10.38 g. of water. The mixture was mixed in a Waring Blendor for 5 min. The emulsion was 28% with respect to polymer, 19% with respect to MIBK, and 1.1% with respect to Ethomid 0/15. This emulsion was diluted to the desired concentration with water as needed.

Application of Emulsion to Fabric

A 3.0% aqueous emulsion of the alloy (weight ratio of TVS to MHS of 1:5) was prepared by the technique described above. It was padded on samples of plain broadcloth and samples of broadcloth which had been previously treated with Fe_2O_3, ZrO_2, a triazone resin, or a triazone resin plus ZrO_2. The samples were cured at 150° C. for 5 min. The spray ratings of the samples before and after a soap-soda boil and a detergent boil are shown in Table IV. All of the samples showed good water repellency after both a soap-soda boil and a detergent boil. Again the samples containing ZrO_2 or Fe_2O_3 gave the highest spray ratings. When ZrO_2 and the alloy were applied to fabric having a triazone resin treatment, greater permanence to the soap and detergent boil was obtained, as shown by final spray ratings of 100. These results were equal to those obtained using the organic-solvent method (see Table II). Best results were obtained with the aqueous emulsion if it was used within several days after its preparation. There was definite indication that polymerization of the emulsified polymers proceeds slowly, for poor results were obtained when the emulsion stood for about two to three weeks.

Use of Zirconyl Acetate Catalyst in the Emulsion

Zirconyl acetate and other zirconium salts have been used in water-repellent treatments [3, 4, 5]. The acetate is supplied commercially as an aqueous solution containing effectively 13% ZrO_2 and 12.5% acetic acid. ZrO_2 applied to fabric by double decomposition was the most effective catalyst for the new alloy, but it required a three-step process. It was found that zirconyl acetate was an effective catalyst when added directly to the aqueous emulsion. By this procedure the process could be carried out in one step.

Samples of broadcloth were padded with 3% aqueous emulsions of the alloy (prepared by the typical procedure given above) containing varying amounts of zirconyl acetate and cured at 150° C. for 5 min. The zirconium was calculated as percent ZrO_2 based on the total weight of the emulsion. The ZrO_2 concentration was varied from about 0.1 to 0.5%. The

spray ratings of the treated samples are shown in Table V. Spray ratings of 90–100 after a soap-soda boil were obtained on samples treated with emulsions containing approximately 0.1–0.4% ZrO_2. These values are lower than found above for ZrO_2 applied by double decomposition.

Use of Zirconyl Acetate Catalyzed Emulsion on Resin-Treated Fabric

Previous work showed the MIBK solutions of the alloy to be very effective when applied to triazone-treated fabric which had been treated with ZrO_2 by double decomposition. The alloy emulsion was equally effective, as previously stated, when applied over ZrO_2-treated triazone fabric. When the zirconyl acetate catalyzed emulsion was applied to triazone-treated fabric, initial spray ratings of 100 were obtained. The ratings averaged 80–90 after the soap-soda boil. This method was not quite as effective as the other two methods, but still very acceptable.

Simultaneous Application of Alloy and Resin Finish

Preliminary experiments were carried out in which the alloy emulsion and a triazone resin were applied to fabric in a one-step process. The triazone and its catalyst were dissolved in the alloy emulsion, which contained zirconyl acetate as a catalyst. The emulsion was padded onto broadcloth and cured at 150° C. for 6 min. The resulting fabric had wrinkle resistance and water repellency (spray rating of 80 after a soap-soda boil). These results indicated the practicability of obtaining crease resistance and water repellency in one step. It is anticipated that this phase of our research will be pursued further.

TABLE V. Effect of Zirconyl Acetate in the Aqueous Emulsion

ZrO_2 as zirconyl acetate, %	Initial spray rating	Spray rating after soap-soda boil
0.13	100	90–100
0.26	100	90–100
0.39	100	90–100
0.52	100	90

Zirconium Butoxide as a Catalyst for the Alloy

Zirconium butoxide as a 50% solution in butanol is commercially available. It was used as a catalyst in the emulsion method in the same manner in which zirconyl acetate was used. Broadcloth samples had excellent spray ratings—100 after a soap-soda boil.

Zirconium butoxide was also found to be an effective catalyst in curing the alloy at room temperature. Samples of broadcloth were padded with a 3% solution of the alloy in ketone containing 0.6% ZrO_2 (as zirconium butoxide). After hanging in a room for 72 hr., the samples had initial spray ratings of 100, and 90–100 after a soap-soda boil. Emulsions containing zirconium butoxide must be used soon after introducing the catalyst because of the rapidity with which it acts.

In preliminary experiments butyl titanate was tried as a catalyst in the same manner as the zirconium butoxide, but it was found to be inferior to the oxide.

Launderability

Table VI shows the spray ratings of samples of plain broadcloth and triazone-treated broadcloth which were treated with a 3% solution of the alloy (weight ratio of TVS to MHS of 1:5) in MIBK using 0.5% ZrO_2 catalyst. These spray ratings were compared with those of two of the better commercial silicones applied to similar fabrics from 3% emulsions by the manufacturers' recommended procedures. A-S refers to a currently used commercial silicone and S-M to a new silicone water repellent recently placed on the market. In all samples except one

TABLE VI. Effect of Home Laundering on Alloy vs. Commercial Silicone Treatments*

Type of treatment	Initial spray rating	Spray rating after home laundering, No. of cycles†			
		2	4	6	6
Alloy	100	80	>80	<70	90
Alloy + 5% triazone	100	<80	80	<80	100
S-M	100	<80	<70	70	80
S-M + 5% triazone	100	<80	80	80	>80
A-S	90	80	>80	<70	80
A-S + 5% triazone	100	<100	<80	80	>80

* S-M and A-S refer to commercial silicones.

† All of the spray ratings were evaluated after the sample had aged for 24 hr., except in final column, where samples were rated again after two weeks.

(A-S on plain broadcloth) the initial spray rating was 100. In all cases the treatment was more resistant to laundering when it was applied over triazone-treated fabric. At comparable add-ons the alloy showed spray ratings equal to or perhaps better than the commercial products after six laundering cycles. It was interesting to note that most of the spray ratings after six launderings increased after the samples were aged for two weeks. The alloy-treated samples had increased the most, from a spray rating of about 70–90 on the plain broadcloth samples and from about 80–100 on the triazone samples.

Samples of broadcloth and percale treated with the alloy and zirconium catalyst were given one wash test according to Fed. Spec. CCC-T-191b, Method 5518. After this rather severe test, which is a 2-hr. wash including a fluoride sour, the spray ratings were zero.

Properties of Fabrics Finished With the Alloy

Fabrics treated with the alloy were not altered in color and generally had a very soft hand. The fabrics with the best hand and permanence to laundering were those treated with alloys of TVS and MHS with weight ratios of 1:2, 1:5, and 1:10 and cured at temperatures of 145–150° C. At this stage of development the 1:5 ratio is a good choice for further investigation.

Some physical properties of 80 × 80 print cloth treated with the alloy in MIBK are shown in Table VII. No ZrO_2 catalyst was used in this experiment.

None of the samples had a strip breaking strength loss greater than 8%. There was only a slight increase in flex abrasion, which was increased approximately three-fold after the soap-soda boil. The flex abrasion of the control, however, was tripled also after the soap boil.

Some physical properties of broadcloth samples treated with a 3% alloy emulsion are shown in Table VIII. These properties are compared with those of an untreated control and with one of the best commercial silicones, designated as S-M. There was a 400% increase in the flex abrasion resistance of the alloy-treated sample (without ZrO_2), and a 165% increase in the sample with ZrO_2. There was a 26% loss in breaking strength of the alloy-treated sample (without catalyst), and only a 6% loss in the sample with ZrO_2. There was a 73% increase in tearing strength of the alloy-treated sample (without catalyst) and a 35% increase in the sample with ZrO_2. There was a significant increase in crease recovery of the sample treated with the alloy (without catalyst). These results compared favorably with those of the commercial S-M silicone.

TABLE VII. Physical Properties of Print Cloth Treated With Alloy by Solvent Method *

Alloy add-on, %	Curing time and temp., min./° C.	Before soap-soda boil: Strip breaking strength (warp), lb.	Before soap-soda boil: Flex abrasion (warp), cycles	After soap-soda boil: Strip breaking strength (warp), lb.	After soap-soda boil: Flex abrasion (warp), cycles
Control	—	47.1	422	45.6	1230
0.8	7/150	46.9	568	41.8	1494
0.8	10/150	44.8	434	44.5	1523
0.8	5/160	45.4	475	43.0	1423
0.8	10/165	43.5	524	43.2	1513

* The weight ratio of TVS to MHS in the alloy was 1:2. No ZrO_2 catalyst was used.

TABLE VIII. Physical Properties of Broadcloth Treated with Alloy by Emulsion Method *

Type of fabric	Flex abrasion (warp), cycles	Strip breaking strength (warp), lb.	Elmendorf tearing strength (warp), g.	Crease recovery, W + F, degrees
Control	375	76.9	873	192
S-M	1476	59.2	1550	244
Alloy, no metal oxide catalyst	1545	56.6	1517	241
Alloy + 0.5% ZrO_2	996	72.0	1180	211

* The weight ratio of TVS to MHS in the alloy was 1:5.

Soiling Characteristics

Preliminary evaluations were made on alloy-treated fabrics as to their wet soiling and oily soiling characteristics. The wet soiling was carried out by agitating the samples in water containing soap, sodium carbonate, and carbon black. The oily soiling was carried out by agitating the samples in xylene containing petrolatum and carbon black. The treated samples and untreated control fabrics picked up little or no carbon as judged by visual observation. One of the new commercial silicones recommended for cotton was tested for oily and wet soiling in the same manner described here. The alloy-treated fabrics soiled less than the fabric treated with the commercial silicone in both oily and wet soiling tests.

Evaluation of Other Fabrics

Preliminary evaluations on water repellency were made on several types of cotton fabrics and modified cotton fabrics using the alloy in MIBK with ZrO_2 catalyst—(a) poplin flameproofed with THPC (tetrakis (hydroxymethyl) phosphonium chloride) and APO (tris (1-aziridinyl) phosphine oxide), (b) cotton sheeting reacted with 2-amino ethyl sulfuric acid, (c) olive drab dyed sateen, and (d) cheesecloth. Spray ratings of 80–100 were obtained after a 1-hr. soap-soda boil. It was interesting to note that cheesecloth treated with ZrO_2 and the alloy would support a pool of water for months without wetting or allowing any water to pass through the open weave.

Acetate rayon, nyon sateen, and Acrilan[4] were also made water repellent by the same method described above. After a 1-hr. soap-soda boil, the spray rating of the rayon acetate was 90; nylon, 100; and Acrilan, 90.

Summary

The simultaneous polymerization of tetravinyl silane (TVS) and methyl hydrogen siloxane (MHS) was carried out using benzoyl peroxide as a catalyst. The most effective method of polymerizing was in methyl isobutyl ketone (MIBK). A weight ratio of TVS and MHS of 1:5 and a temperature of 80° C. for about 90 min. are satisfactory for use of the finish. The resulting blended polymer when deposited on cotton fabric is referred to as an alloy of TVS and MHS, since the product is a blend of two polymers and no evidence was found to support copolymerization of the components.

The alloy was applied to fabrics by several different methods. Two of the most effective methods consisted of depositing ZrO_2 (Fe_2O_3 was just as effective but gave fabrics a yellow color) on the fabric by double decomposition and then applying the alloy from either an organic solvent, preferably MIBK, or an aqueous emulsion. Both of these methods, however, required several steps. A satisfactory one-step procedure was developed by adding catalysts such as zirconyl acetate or zirconium butoxide to either the organic solution or aqueous emulsion of the alloy. Spray ratings of 100 before and about 90 after a soap-soda boil were obtained by both the solvent method and the emulsion method.

The alloy finish was even more effective when applied to resin-treated fabrics. Preliminary experiments indicated that the alloy and amino resins could be applied from a single bath by a one-step process.

Preliminary experiments indicated that durable water repellency might be obtained by padding with an MIBK solution of the alloy containing zirconium butoxide as a catalyst and curing at room temperature for several days, no heat curing being necessary.

[4] Chemstrand trademark.

Acknowledgments

The authors wish to express their appreciation to Mrs. Julia Sloan and Mr. Henry Allen for the physical textile tests and to Mr. Walter M. Cholewczynski for preparation of samples with commercial water repellents.

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Cotton Cross-Linked at Various Degrees of Fiber Swelling[1]

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Abstract

Wet and dry density measurements were made on a wide variety of wash-and-wear cotton fabrics and some interpretations of these values are given. Methylenated cotton was selected for more extensive fundamental study because of the simplicity of the formaldehyde cross link and the fact that formaldehyde can be reacted with cotton under greatly different conditions. Formaldehyde was used to cross link cotton print cloth at various degrees of fiber swelling by reacting in systems ranging from completely aqueous to anhydrous using hydrochloric acid as catalyst. The amount of water in the system at the time of reaction is related to the extent of fiber swelling. The extent of swelling at the time of cross-linking and the extent of cross-linking influence wet density, which may be considered to be a measure of the water swellability of a fiber. Cross-linking tends to fix or stabilize a fiber in a given state of swelling; the stabilization is more effective when the cross-linking is done in nearly anhydrous systems. The state of swelling at the time of cross-linking modifies moisture regain, water of imbibition, dyeability, and wet and dry wrinkle recovery. There seems to be an optimum water content in the reaction system at the time of cross-linking for maximum dry and wet wrinkle recovery. As the water content in the reaction system is increased beyond the optimum, the amount of dry wrinkle recovery becomes much less than wet wrinkle recovery. This phenomenon leads to vastly different wash-and-wear ratings of fabric.

A mechanism is presented diagrammatically to explain wet and dry wrinkle recovery. The mechanism is based upon hydrogen-bond cross links, covalent-bond cross links, and the position of the two types of cross links.

ALTHOUGH wrinkle resistant cotton fabrics have been known for about 30 years, many of the basic principles for imparting wrinkle recovery are not too well understood. The wrinkle recovery and wash-and-wear characteristics of a textile are affected by its construction and by the construction of the yarns of which it is composed. However, the properties of the fiber which make up the yarn and fabric have, perhaps, an even greater influence on wrinkle recovery and wash-and-wear properties. Cross-linking within the fiber seems to have been accepted by most researchers as the basic requirement for wrinkle recovery. It provides an excellent way of changing many of the properties of cotton fiber. The physical properties of cross-linked goods are quite well known, but the principle of producing physical changes with cross links within the microstructure of the fiber, which is actually responsible for the fiber properties, is not too well defined.

Differences have been observed between the wrinkle recovery of cotton fabrics finished by the pad, dry, and cure process and the wrinkle recovery of fabric finished while swollen in mercerizing strength alkali solution. The first of these processes, which is often thought of as reacted in the collapsed state, imparts wet and dry wrinkle recovery. The second-named process has been observed to impart only wet wrinkle recovery. Because of the results obtained at these two extremes, considerable curiosity was aroused about the properties and relative merits of fabric cross-linked at various degrees of fiber swelling. It was reasoned that a study of cotton fabric cross-linked at various states of swelling might provide some basic concepts about wash-and-wear fabrics and perhaps aid in providing better quality products.

The purpose of this paper is to report the experi-

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

mental results obtained by cross-linking cotton cellulose at various degrees of fiber swelling and to report some theoretical interpretations of the observed facts to explain wet and dry wrinkle recovery. In this study 80 × 80 print cloth was reacted with known types of wash-and-wear finishing agents. Wet and dry wrinkle recovery and wet and dry fiber densities were determined. These are reported and discussed in the experimental portion of this paper. From these first results, which represented cross-linking at the two extremes—collapsed and swollen—it was apparent that interesting results would be obtained if a system could be found to provide cross-linking, not only at the two extremes, but also at several points in between the extremes. The known methods for reacting N-methylol type compounds with cellulose are not suitable for cross-linking cotton at a number of stages of fiber swelling. Diepoxy compounds could possibly be used, but these materials are too likely to deposit polymer concurrently with the cross-linking reaction and that would make the study more complex. Formaldehyde appeared to be the most suitable compound for use in this study, for it has been reacted with cellulose in many instances by the dry and cure process and by a limited number of researchers in aqueous solutions [5, 9, 10, 12]. Additionally, the cross link formed with formaldehyde is a simple methylene bridge [15]. By progressively replacing larger amounts of water in an aqueous system with a water-miscible nonswelling liquid, it should be possible to react formaldehyde with cotton under varying degrees of fiber swelling. For theoretical considerations of cross-linking, formaldehyde has other advantages over the usual cross-linking agents. It is equally as effective, per degree of substitution, as the epoxy and N-methylol type agents in imparting wrinkle recovery, and at the same time the methylene bridge has little effect on the the gross weight of the textile. This weight factor is especially important in density studies. Also, the methylene bridge does not carry functional groups to influence studies of moisture regain, water of imbibition, and dyeing characteristics.

Materials and Methods

All of the work reported herein was done on 80 × 80 print cloth. It was a desized, scoured, and bleached cloth weighing 3.1 oz./sq. yd. The finishing agents used were tris (1-aziridine) phosphine oxide [APO]; dimethylol cyclic ethyleneurea [DMEU], Rhonite R-I;[3] methylolmelamine [MF], Resloom HP;[3] fresh formic acid colloid of methylolmelamine [FAC-MF]; a commercial triazone [triazone], Permafresh LCR;[3] a commercial epoxide [epoxide], Eponite 100;[3] formaldehyde; and glycerol-dichlorohydrin [GDC]. The formaldehyde was a commercial grade formalin containing 36.2% formaldehyde and 12% methanol as stabilizer. The GDC was a mixture of 75% α, β and 25% α,γ-glyceroldichlorohydrin.

All of the above finishing agents except the GDC were applied by the usual pad, dry, and cure procedure. The catalysts and the cure temperatures are given in the experimental section. GDC and formaldehyde were reacted in "solution." The GDC was reacted by first padding the fabric in a solution of GDC; then, while still wet, it was immersed in 20% sodium hydroxide solution to promote reaction and finally washed and dried [13]. Formaldehyde was reacted in solution by immersing the print cloth in a solution containing formaldehyde and hydrochloric acid, then rinsing and drying. The details of the formaldehyde treatments are given in the experimental section below.

The wrinkle recovery angle, WRA, was determined on the dry and wet fabrics. The dry wrinkle recovery was done according to the ASTM, Monsanto method [2]; the wet was done according to the procedure of Lawrence and Philips [7]. Formaldehyde determinations were made by hydrolyzing the methylenated cotton with sulfuric acid and subsequent colorimetric estimation of the formaldehyde in the distillate with phenylhydrazine [3]. Moisture regain was obtained by first heating the samples for 2 hr. at 30° C., then equilibrating for 72 hr. at 65% relative humidity and 70° F. The equilibrated samples were weighed and then dried for at least 4 hr. at 105° C. and again weighed. The moisture regain was calculated from the change in weight due to moisture and the weight of the dry fabric.

Experimental and Discussion

Dry and Wet Densities of Wrinkle-Resistant Cotton Fabrics

The density of a cotton fiber is the mass per unit volume; it is usually expressed in terms of g./cc. The density is dependent upon the amount of crys-

[3] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

talline and amorphous cellulose. In the current studies densities determined on samples that had been freed of gas and moisture are termed dry densities. Wet densities were obtained by measuring the g./cc. of fiber or fabric that had been swollen in water. This involved first swelling in water, then solvent exchanging from water to methanol to acetone to carbon tetrachloride, and finally equilibrating the cotton in the gradient column containing a moist cotton cord. The procedures reported by Orr et al. [11] have been followed in determining both dry and wet densities. The dry density, which is the weight of 1 cc., is related to the degree of openness or compactness of the dry fiber. Wet density may be considered a measure of the swellability of a fiber, for in this case, the density or weight of 1 cc. is that of water-swollen fibers. Dry density of acetylated cotton has been shown to decrease linearly as the degree of substitution increases [11]. Steele [14] found that dimethylolurea finishes, which cross link cotton, decrease the dry density more than monomethylolurea derivatives at the same add-on, which cannot cross link.

The treated fabrics used for density measurements in the current study are described in Table I. The finishing agents listed represent the known types of finishes in current use for making wrinkle resistant fabrics. The wet and dry densities, as well as wet and dry wrinkle recovery, were determined on most of the fabrics at two levels of finish add-on.

There are some interesting points to note about the density measurements. In all cases the dry density decreased as the weight of finish add-on increased. Cross-linking the fiber while in water or in an alkali solution produced fabric with somewhat lower dry densities. All the dry densities show that cross-linking fixes the dry fiber in a more open or less dense condition than exists in unreacted cotton fiber. The wet densities are of considerable interest too. An increase in add-on of resin finish caused an increase in wet density in every case. The wet density at the lower add-on of finish is quite low, indicating the fibers have ability to swell in water; according to densities, the ability to swell is even greater than that of untreated control fabric. The higher wet densities for the more highly reacted fabrics could be the result of the filling of existing voids within the fiber by the added compound, or reaction of the cross-linking agents with the cellulose, thereby restricting fiber swelling in water. This latter possibility seems most likely because dry densities would have been increased if the compounds or resins merely filled existing voids. The wet and dry density values support the idea that cross-linking fixes the cotton fiber in a more open or less compact condition. Both wet and dry density values also indicate that the state of fiber

TABLE I. Dry and Wet Densities of Wrinkle-Resistant Cotton Fabrics

Finishing agent	Catalyst used	Reaction conditions	Apparent weight add-on, %	WRA (W + F)		Density	
				Dry	Wet	Dry	Wet
DMEU	H-7	dry, cure	1.8	260	236	1.536	1.472
DMEU	H-7	dry, cure	5.3	287	301	1.531	1.522
APO	None	dry, cure	1.7	191	202	1.536	1.480
APO	None	dry, cure	5.3	228	249	1.524	1.512
APO	$Zn(BF_4)_2$	dry, cure	1.6	190	222	1.542	1.477
APO	$Zn(BF_4)_2$	dry, cure	5.3	242	257	1.536	1.506
MF	H-7	dry, cure	2.9	223	222	1.544	1.477
MF	H-7	dry, cure	6.9	275	264	1.542	1.532
FAC-MF	Formic acid	dry, cure	2.1	216	216	1.542	1.480
FAC-MF	Formic acid	dry, cure	5.5	263	248	1.536	1.532
Triazone	H-7	dry, cure	3.5	266	231	1.532	1.494
Triazone	H-7	dry, cure	6.5	272	280	1.532	1.502
Epoxide	$Zn(BF_4)_2$	dry, cure	2.6	195	218	1.534	1.486
Epoxide	$Zn(BF_4)_2$	dry, cure	7.5	263	258	1.533	1.513
HCHO	$MgCl_2+AlCl_3$	dry, cure	<1.0	284	272	1.532	1.506
HCHO	HCl	solution	0.4	182	302	1.525	1.460
GDC	NaOH	solution	<1.0	226	255	1.524	1.462
Untreated control				200	194	1.544	1.505
Mercerized fabric				192	217	1.534	1.476

swelling at the time of cross-linking influences the final state of openness existing in the cross-linked fiber.

Cross-Linking of Print Cloth With Formaldehyde Under Conditions Ranging From Anhydrous to Completely Aqueous

Eight solutions were made up containing formaldehyde, hydrochloric acid, and various amounts of water for use in cross-linking cotton cloth. The amount of water in the systems was varied by substituting acetic acid for water; in two cases acetic anhydride was added also to react with water that was introduced with the aqueous acid and formaldehyde so as to reduce the total amount of water in the system. Water is a good swelling agent for cotton, whereas acetic acid is relatively much less effective for this purpose. Acetic acid does have some swelling action on cotton, for it is used in the acetylation process to swell the fiber and permit reaction. The purpose of progressively decreasing the amount of water in the systems was to provide systems which had progressively less swelling action on cotton fabric. It is very likely, however, that the systems containing very small proportions of water have a greater swelling effect per unit of water than the systems which contain large proportions of water. By reacting with formaldehyde in the systems, fabric which was cross-linked at various degrees of fiber swelling could be prepared for subsequent study. The compositions of these solutions are shown in Table II.

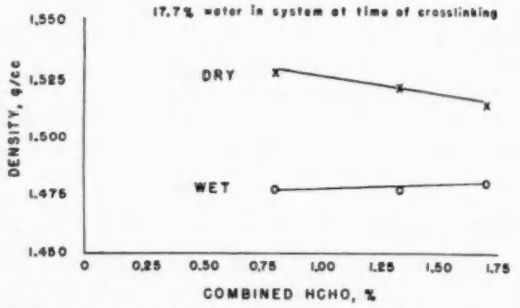

Fig. 1. Influence of amount of combined HCHO upon wet and dry densities of cotton fabric.

The above solutions were used to treat print cloth by immersing samples of the fabric in the solution at about 28° C. Strips of cloth, measuring 16 × 20 in., were covered with a loose weave glass fabric of the same dimensions and then the two fabrics were rolled loosely. The entire roll was immersed in the desired HCHO—HCl solution for a predetermined time. About 7 l. of solution was used in each case. Several samples of fabric were treated with each solution so as to obtain fabrics with various amounts of combined formaldehyde. It was desired to produce fabrics with combined formaldehyde contents ranging from about 0.2% up to about 1%. The treated fabrics were washed for about 3 hr. in running tap water at a pH of about 9.5 and then line-dried.

Formaldehyde reacted with the cotton very slowly in Solutions 1 and 3, shown in Table II. The combined formaldehyde was about 0.4% after five days reaction. To get a sufficient degree of reaction in these systems, it was necessary to raise the formaldehyde and hydrochloric acid concentrations to that in Solutions 2 and 4. Reaction also went very slowly in the completely anhydrous system, shown as Solution 8. In this case fabric that was oven-dried before entering the reaction medium contained only

TABLE II. Formaldehyde Solutions Used to Cross Link Cotton at Various Degrees of Fiber Swelling

Solution no.	Calculated amount of water in the final system, %*	HCHO, %	HCl, %	Acetic acid, %	Acetic anhydride, %
1	92.7	3.6	3.7	—	—
2	75.3	7.5	17.2	—	—
3	67.7	3.6	3.7	25	—
4	68.0	7.5	17.2	7.3	—
5	42.7	3.6	3.7	50	—
6	17.7	3.6	3.7	75	—
7	9.0	3.6	3.7	60†	20
8	0.0	3.6	3.7	8†	72

* The amount of water indicated includes a small amount of methanol which was in the formaldehyde solution as a stabilizer.
† The percent acetic acid here does not include that formed from the reaction of water and acetic anhydride.

0.2% combined formaldehyde after five days of reaction, and the fabric was quite weak. The initial rate of reaction was much greater when air-equilibrated fabric was used in the reaction. This indicates the mechanism for methylenation of cellulose is through a methylene glycol structure. But when air-equilibrated fabric was reacted in the anhydrous solution the fabric was highly degraded; too degraded to be of much value in this study. The reaction went most rapidly in Solutions 2, 4, 6, and 7. The fabrics produced by reaction in the various systems will be described in the remaining experimental portion of this paper.

Dry and Wet Densities of Cotton Fabric Cross-Linked with Formaldehyde in Systems Containing Various Amounts of Water

Dry and wet density measurements were made on the print cloth which had various amounts of combined formaldehyde and which had been reacted in the systems ranging from anhydrous to completely aqueous. These values confirm and extend the information reported above, which was obtained from a wide variety of wrinkle-resistant fabrics. Here again the dry densities decreased as the weight add-on of reactant increased; the wet densities increased slightly as add-on increased. This can be seen in Figure 1. Also, the dry densities are greatest for those fabrics reacted in systems containing the least amount of water. This is good evidence that cross-linking tends to fix the fibers in a state of swelling in which they existed at the time of cross-linking. Figure 2 shows that fibers cross-linked in the system containing 8% water had a dry density of 1.534 g./cc. as compared to 1.518 g./cc. for fabric cross-linked in a completely aqueous system. The densities used for developing the curve in Figure 2 were obtained directly from fabric that contained exactly 0.8% combined formaldehyde, or were interpolated values from fabric containing other than 0.8% formaldehyde. For example, fabric cross-linked in 75% water did not contain exactly 0.8% combined formaldehyde, but fabrics were available that contained 0.73 and 0.85%. Densities were run on both of these fabrics; then these values were used to interpolate a density for fabric with 0.8% formaldehyde. This same technique was used below in other studies of the fabrics.

The wet densities of fabric containing 0.8% combined formaldehyde and cross-linked at different degrees of fiber swelling showed the same trend as observed for the dry densities. The wet densities were the greatest for the fabrics cross-linked in systems containing the least amount of water.

Dyeing Properties of Fabric Cross-Linked With Formaldehyde in Systems Ranging from Anhydrous to Completely Aqueous

Numerous samples of the print cloth, which had been reacted in the solutions described in Table II, were dyed with a direct dye (Chlorantine Fast Blue 4GL). The dyeing was carried out in a bath containing 2% dye and 20% sodium chloride, calculated on the weight of the cotton. The bath was 30 times the weight of the fabric samples. Three-inch square samples of fabric were placed into the boiling bath for 30 min., then rinsed in tap water for 1 hr. There was a vast difference in the color intensity of some of the dyed samples.

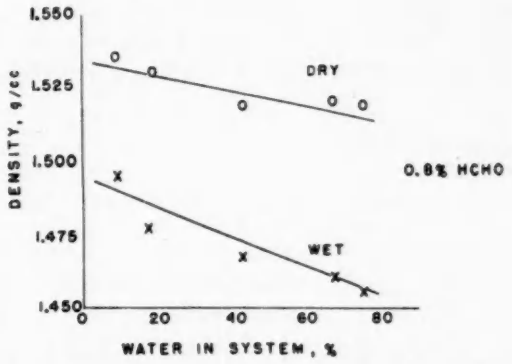

Fig. 2. Influence of amount of water in system at time of cross-linking upon wet and dry densities.

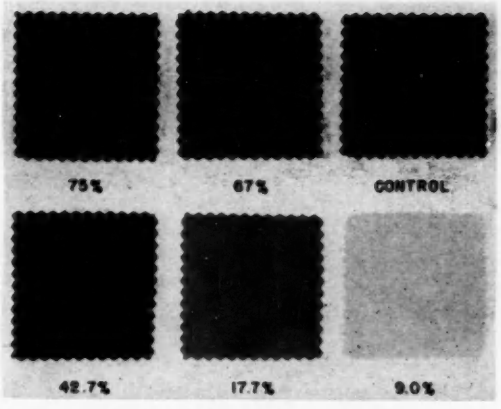

Fig. 3. Bleached print cloth cross-linked with 0.6% HCHO in system containing various percentages of water, then dyed with Chlorantine Fast Blue 4GL.

The intensity of a direct dyeing on a cellulose fiber is usually associated with the accessibility and availability of the hydroxyl groups. Chemical reaction and steric hinderance of hydroxyl groups may hinder dyeing and result in dye-resist. For example, dye-resist is accomplished by reducing the number of hydroxyls by acetylation. Dye-resist has also been observed on methylenated cotton fabric [4]. In this case the dye-resist was considered to be due to cross-linking of the cellulose. It was suggested that the progress of the reaction could be followed by observing the reduction in the capacity of the cotton for taking up the direct dye. The present work shows that dye-resist of methylenated cotton fabric is due to more than just cross-linking. In related work, F. C. Wood indicated that the amount of moisture present at the time the cellulose was methylenated determined whether the product was of the dye-resisting or dye-absorbing character [18]. This was also found to be true in the work reported here. Figure 3 illustrates differences in dyeings obtained on fabrics which contained the same amount of combined formaldehyde. Each fabric contained 0.6% formaldehyde, but they had been reacted in systems containing different amounts of water. The fabrics cross-linked in systems containing 68% or more water dyed slightly darker than untreated control fabric, whereas with 43% water in the cross-linking system, the dyeing was nearly as intense as the control. There was considerable dye-resist with the fabrics cross-linked in the systems containing 18% or less water. It is true, as reported earlier, that the extent of cross-linking influences dye-resist; however, the dye-resist is readily apparent only when fabrics are cross-linked in systems containing a low percentage of water. There was little difference in the dye-resist of fabrics containing 0.3% and 0.8% combined formaldehyde when cross-linked in the aqueous system. The differences in dye intensities illustrated in Figure 3 must be due to differences in the submicroscopic structures within the fibers because all the fabric specimens contained essentially the same amount of combined formaldehyde. The dye molecule is relatively large; therefore, rather large openings must be available for dye pentration. According to the color intensities, the opening or pore sizes within the fiber were adequate to freely admit the dye molecules when the fabrics were cross-linked in systems containing about 43% or more water; the reduced dye accessibility became quite pronounced when the fabrics were cross-linked in the systems containing 18% or less water. These observations do not necessarily imply that there was an abrupt change in pore size, although there was an abrupt change in dye accessibility. As long as the pore size was just great enough to admit the dye, intense color was observed, but as soon as the pore size became too small to admit the dye, as in the case of the two fabrics on the lower right of Figure 3, there was a sharp increase in dye-resist.

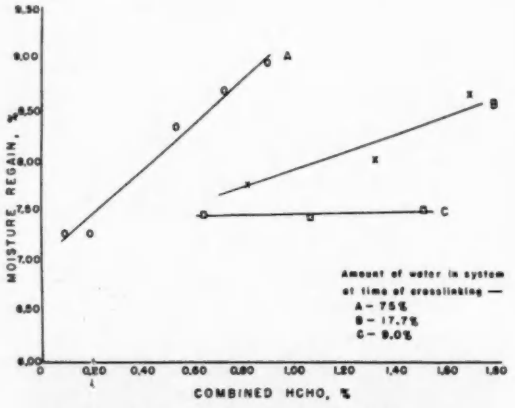

Fig. 4. Effect of amount of cross-linking upon moisture regain.

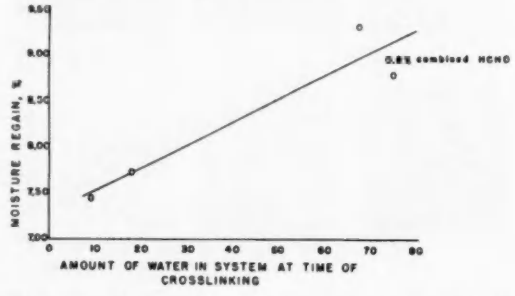

Fig. 5. Influence of extent of swelling at the time of cross-linking upon moisture regain.

Moisture Regain of Cotton Fabric Cross-Linked With Formaldehyde in Systems Containing Various Amounts of Water

The amount of moisture absorbed from the air by a fabric is dependent upon fabric and yarn structure, the humidity of the atmosphere, the nature of the fibers in the fabric, and perhaps other factors. By keeping the first three factors constant, moisture regain becomes a useful means of studying changes in the fiber. The moisture regain of cellulose fibers has been shown to be related to the average degree of

lateral order or crystallinity of the cellulose [6]. That work was done on unmodified cellulose fibers, including cotton and mercerized cotton. In such studies the regions inaccessible to water vapor were considered crystalline regions. This was verified by x-ray measurements. When cross-linked cotton fibers are being considered, the inaccessible regions are not necessarily crystalline; these regions may be made inaccessible by other physical restrictions. The moisture regain of cotton fibers and cross-linked cotton fibers is related to the internal surface area of the fiber. It is mainly the hydroxyl groups in the accessible surfaces that bind water. The hydroxyl groups in the inaccessible (to water vapor) regions, whether made inaccessible by hydrogen bonding in the crystalline regions or by primary valence cross links in initially accessible areas, are not available for water absorption, and this results in reduced moisture regain.

Moisture regain was determined on a number of fabrics cross-linked with the formaldehyde in the solutions described in Table II. The results obtained on a series of fabrics treated with Solutions 2, 5, and 7, which contained 75, 17.7, and 9% water respectively, are shown in Figure 4. The curves show that the moisture regain increases as the amount of combined formaldehyde increases, except for the fabric cross-linked in the system containing 9% water, where moisture regain remained about constant. These results indicate that cross-linking of the swollen fibers tends to fix the fibers in the swollen condition and therefore increase the internal surface area. The very low degrees of substitution are less effective than extensive substitution in preventing collapse of the swollen fiber when it is dried.

The moisture regain of all of the fabrics cross-linked in solutions described in Table II was greater than that of untreated control fabric. This was due to the fact that acetic acid has a swelling effect on cotton, although relatively much less than that of water. All the fabrics listed in Table I which were produced by the dry and cure technique had lower moisture regain than the untreated control fabric. This means that the small amount of water in these fabrics, at the time of cross-linking, had less swelling action than the system of Table II, containing acetic acid and 9% water.

The influence of the amount of water in the system at the time of cross-linking upon moisture regain is illustrated in Figure 5. With 75% water in the cross-linking system, the moisture regain was 9.44%, and this value decreased as the amount of water in the system decreased to 9%, where the moisture regain was 7.45%. Each of the fabrics used in Figure 5 to develop the curve contained 0.8% combined formaldehyde so as to eliminate the effects of extent of cross-linking.

Water of Imbibition of Cross-Linked Cotton

When cotton is wet in water, it imbibes a considerable volume of the water. The imbibition is accompanied by a large increase in volume of the fiber, caused by a considerable internal pressure. Much of the water can be removed by centrifugal force, but a certain amount remains imbibed. The amount remaining after centrifuging is dependent upon the chemical and physical characteristics of the fiber. The amount of water imbibed by cotton fiber can be altered by modifying the nature of the accessible regions or by altering the amount of accessible regions. Chemical modification, cross-linking, and mercerization alter the amount of water imbibed [16]. Water of imbibition is substantially different from moisture regain at 65% relative humidity. Whereas moisture regain is related to the availability of the hydroxyl groups in the internal surface of a relatively unswollen fiber, imbibition is related to the accessible internal area of a highly swollen fiber. However, in both cases the sorbed water is held by secondary valence forces.

The procedure used for determining water of imbibition was essentially that used by Welo et al. [16]. One-half-gram samples of the print cloth were cut into 1-in. squares and placed into about 50 ml. of boiling distilled water for a few minutes; then the water and fabric were allowed to equilibrate at room

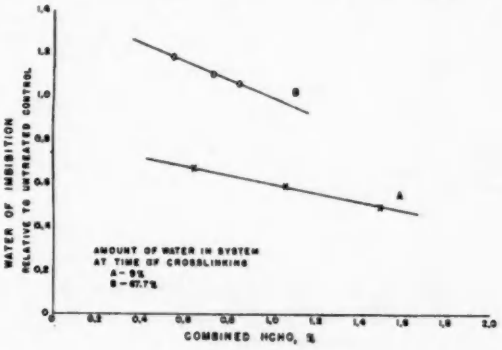

Fig. 6. Influence of extent of cross-linking upon water of imbibition.

temperature for 24 hr. The samples were placed in perforated steel tubes and centrifuged for 20 min. in a closed system at 7,500 rpm, using a Serval Angle Centrifuge.[3] The wet samples were weighed, then dried for 4 hr. at 105° C. and again weighed. The difference in dry and wet weight was calculated as water of imbibition.

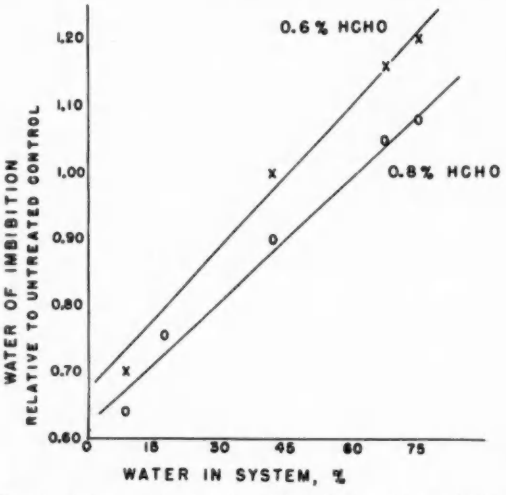

Fig. 7. Influence of state of swelling at time of cross-linking upon water of imbibition.

Water of imbibition was determined on a number of samples of print cloth treated with the formaldehyde solutions described in Table II. The extent of cross-linking, as measured by the amount of combined formaldehyde, had a definite effect upon the amount of water imbibed. Curve A of Figure 6 illustrates the decrease in imbibition that accompanies an increase in extent of cross-linking. In this particular case the fabric was cross-linked in the system containing 9% water, which is a relatively nonswelling system. The retained water at 0.65% combined formaldehyde was 67% of that of the control whereas, with 1.07% combined formaldehyde, the imbibed water was only 59%. This type relationship is illustrated again in Curve B. This curve was obtained with fabric cross-linked in a system containing 68% water. The fabric containing 0.54% formaldehyde retained about 20% more water than untreated fabric. It is apparent from comparison of Curves A and B of Figure 6 that cross-linking does not necessarily reduce the amount of water imbibed, as might have

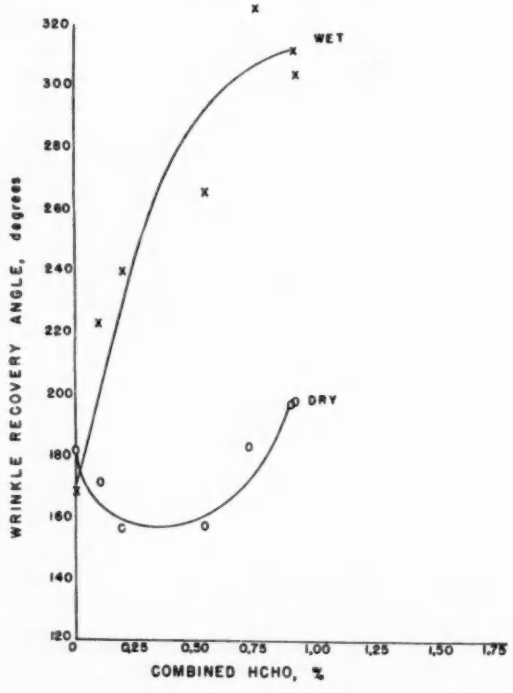

Fig. 8. Wrinkle recovery of fabric cross-linked in aqueous solution.

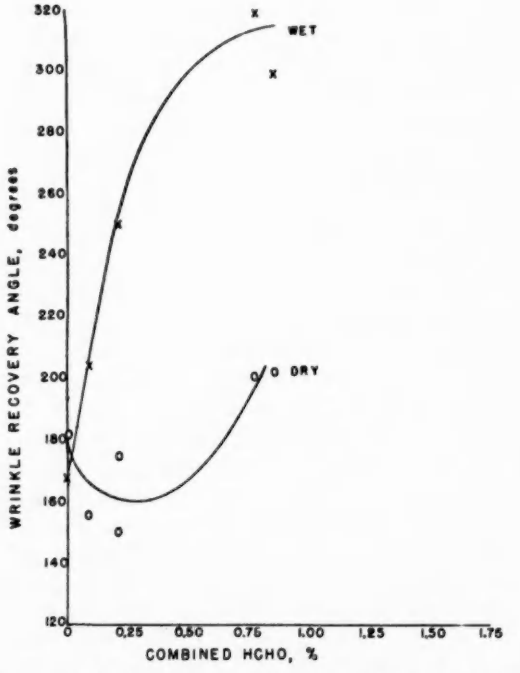

Fig. 9. Wrinkle recovery of fabric cross-linked in system containing 68% water.

been assumed from the literature. Figure 7 shows the influence of extent of swelling at the time of cross-linking upon water of imbibition. In order to eliminate variables due to extent of cross-linking, fabrics containing a specific amount of combined formaldehyde at the various states of fiber swelling were compared. The comparisons were made at 0.6% and at 0.8% combined formaldehyde. In both cases the state of fiber swelling at the time of cross-linking is by far a more influential factor on water of imbibition than the extent of cross-linking.

The Effects of Fiber Swelling at the Time of Cross-Linking on Wrinkle Recovery and Wash-and-Wear Qualities

The relative importance of dry and wet wrinkle recovery has not been fully assessed. Up to about three years ago, little attention had been given to wet wrinkle recovery. Before then, the mention of wrinkle recovery generally implied dry wrinkle recovery. However, the resin-finished fabrics in general use then did have good wet wrinkle recovery. Note that all the fabrics listed in Table I that were produced by the dry and cure technique had wet and dry wrinkle recovery. Just a few months ago, Williams [17] pointed out from his studies on rayon that wet wrinkle recovery is the predominant requirement for elimination of distortions caused by laundering and that wet wrinkle recovery must be present for good wash-and-wear performance. He considered wet wrinkle recovery as important as dry wrinkle recovery in wash-and-wear goods.

Dry and wet wrinkle recovery and wash-and-wear qualities were determined on formaldehyde cross-linked fabrics methylenated with the solutions described in Table II. These fabrics, as pointed out above, were cross-linked in systems ranging from anhydrous to completely aqueous. Since wet and dry densities, dyeings, moisture regain, and water of imbibition all indicate that the cross links tend to fix the fibers in a state of swelling that they are in at the time of reaction, the wet and dry wrinkle resistance can be related to fiber swelling at the time of cross-linking. There are two important factors which influence wet and dry wrinkle recovery: the amount of combined formaldehyde (which is, no doubt, related to extent of cross-linking) and the amount of fiber swelling at the time of cross-linking. The effects of both factors can be seen in Figures 8, 9, 10, 11, and 12.

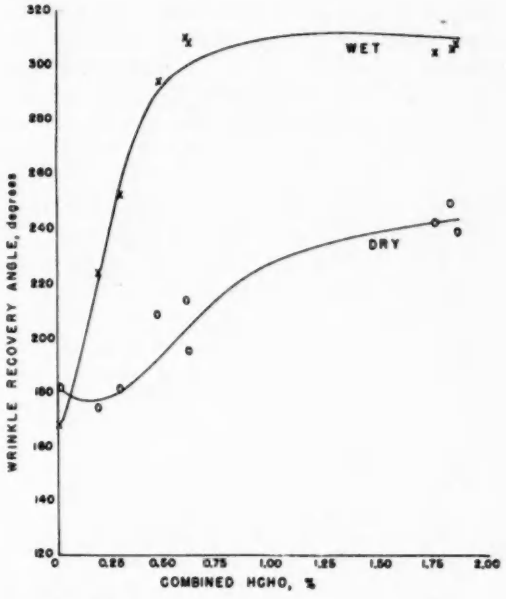

Fig. 10. Wrinkle recovery of fabric cross-linked in system containing 42.7% water.

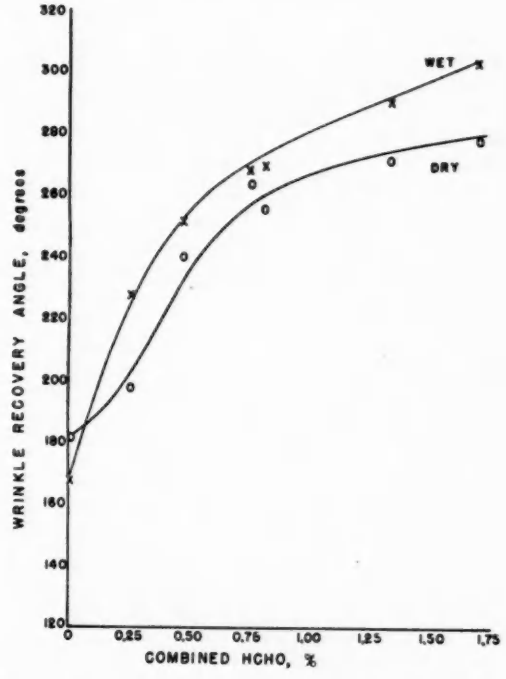

Fig. 11. Wrinkle recovery of fabric cross-linked in system containing 17.7% water.

Figure 8 describes the wrinkle recovery properties of fabric methylenated in a completely aqueous system—the system contained only water besides the acid catalyst and formaldehyde (Solution 2 of Table II). Three things should be noted here: extremely high wet wrinkle recovery, very low dry wrinkle recovery and an initial decrease in the observed dry wrinkle recovery at a very low degree of cross-linking (small amount of combined formaldehyde). Figures 9 and 10, which describe fabrics with 68% and 42.7% water in the cross-linking system, show a gradual transition in the observed wrinkle recovery, the wet showing a slight decline per unit of cross-linking while the dry wrinkle recovery is increasing. With 17.7% and less water in the system, a high degree of wet and dry wrinkle recovery was obtained, as illustrated in Figures 11 and 12. It is interesting to note that the wet wrinkle recovery was good in all of the systems. Wet wrinkle recovery was obtained at lower degrees of substitution than dry recovery.

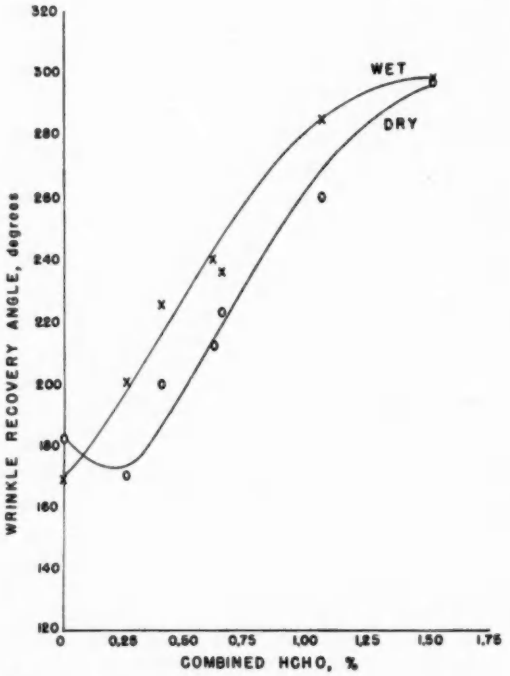

Fig. 12. Wrinkle recovery of fabric cross-linked in system containing 9.0% water.

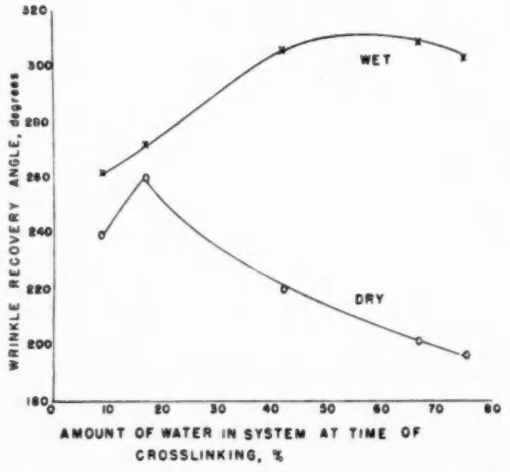

Fig. 13. Wrinkle recovery of fabrics cross-linked with 0.8% combined HCHO at various degrees of fiber swelling.

The effect of fiber swelling at the time of cross-linking on wrinkle recovery is also illustrated in Figure 13. In this figure, the results are given for fabrics which contained 0.8% combined formaldehyde. Each fabric was cross-linked at a different degree of fiber swelling. In the more anhydrous systems, where the fibers were cross-linked in a rather collapsed state, wet and dry wrinkle recovery was imparted. There was a considerable increase in wet wrinkle recovery and a considerable decrease in dry wrinkle recovery as the cross-linking systems became more aqueous.

The wash-and-wear qualities of the various cross-linked fabrics are related to wet and dry wrinkle recovery, and the wrinkle recovery as shown above is dependent upon the extent of fiber swelling at the time of cross-linking. Wash-and-wear qualities were rated after three types of laundry procedures. The laundry procedures were essentially the same as AATCC tentative test procedure 88-1958 [1]; the

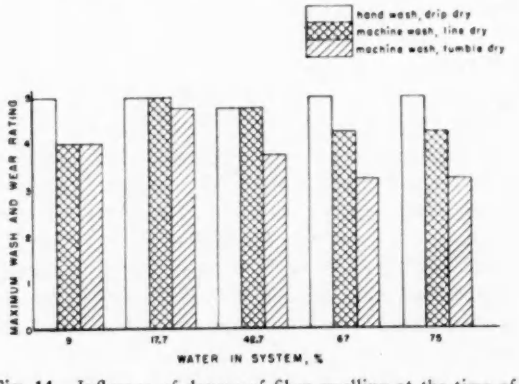

Fig. 14. Influence of degree of fiber swelling at the time of cross-linking upon wash-and-wear ratings.

main difference was in the number of times laundered before rating. In the current work, the fabrics were hand washed and allowed to drip dry; then machine washed, centrifuged and line dried; then machine washed and tumble dried. The fabrics were rated after each of the laundry procedures; Figure 14 summarizes the results. The amount of water in the system at the time of cross-linking which determines the final state of the fiber structure had a great influence upon the wash-and-wear properties of the cotton fabrics. Systems which had a small amount of water produced fabrics with both dry and wet wrinkle recovery, and these fabrics exhibited the best wash-and-wear properties. The ratings were good, regardless of the method of washing. Fabrics cross-linked in the systems containing large amounts of water exhibited good drip-dry properties, but the tumble-dry properties were poor. These fabrics were shown above to have good wet wrinkle recovery and poor dry resistance. From these results it can be seen that dry wrinkle recovery is needed for good tumble dry properties. The value of dry wrinkle recovery in the absence of wet could not be investigated because all the fabrics with dry recovery also had good wet recovery. It would be expected, however, that fabrics with only dry wrinkle recovery would have good wash-and-wear properties when laundered by either of the procedures, especially by the tumble-dry procedure.

A Cross-Linking Mechanism to Explain Wet and Dry Wrinkle Recovery

The above observations, and others cited below, have been used in developing simplified diagrams to illustrate what the authors believe to be the fundamental role of cross links in wet and dry wrinkle recovery. Most workers in this field have accepted cross-linking as a necessity for imparting wrinkle recovery. The accepted cross links are produced through covalent or primary valence bonds. This is about as far as one generally goes, although a number of workers have indicated that hydrogen bonding is involved. The present authors have been unable to visualize just how cross-linking through primary valence bonds alone could account for all the observed facts. It seems that there are three very important factors to be considered in explaining wrinkle resistance: cross-linking through primary valence bonds, cross-linking through secondary valence bonds, and the location of the cross links.

First consider secondary valence bonds—hydrogen bonds in this case. Ordinary cotton fabrics possess some natural wrinkle resistance. This is often neglected, since unmodified fabric is usually the reference standard for wrinkle recovery tests. However, it must be remembered that the minimum wrinkle recovery angle (W + F) as measured on the Monsanto wrinkle tester is about 90°, yet a cotton fabric, like print cloth, has a dry (equilibrated at 65% RH) wrinkle recovery angle of about 170°. This represents a considerable degree of wrinkle recovery. A quite significant point is that the generally observed wrinkle recovery can be increased by merely drying; also, it can be reduced by equilibrating at very high relative humidities. By thorough drying over P_2O_5, the dry wrinkle recovery angle of cotton print cloth was brought up to 200° [8]. Certainly this wrinkle recovery was not brought about by covalent or primary valence cross links. Hydrogen bonds appear to be the only good explanation for this fact.

The same print cloth mentioned above had a wet wrinkle recovery angle of 155°. The decrease in the wrinkle recovery of dry cotton brought about by wetting in water was caused by destroying some of the hydrogen-bonded cross links.

To illustrate the role of cross-linking through hydrogen bonds, cross-linking by primary valence bonds, and the position of the cross links, consider these factors in relation to two cellulose chains in the secondary wall of the cotton fiber. The two have been selected to represent a relationship that could exist between two molecules that extend from one semicrystalline region through a region of high accessibility to another semicrystalline region. The region described as semicrystalline might also be referred to as a region with moderate degree of lateral order in contrast to the highly accessible area. The semicrystalline region referred to here is then a region existing between the highly crystalline and highly accessible regions. Because of the length of the cellulose molecules existing in cotton and because of the frequency of occurrence of the regions of high and low lateral order, it is now accepted that a single molecule may even extend through a number of accessible and nonaccessible regions within the microfibril. These highly accessible and less accessible regions occur between chains within the same microfibrils, between chains of adjacent microfibrils, and between chains of adjacent lamellae or layers.

The changes in hydrogen-bonded cross links ac-

companying the changes in wrinkle recovery of cotton are illustrated in Figure 15. For simplicity, Diagram A represents hydrogen bonding occurring between two cellulose chains in equilibrium with atmospheric moisture. The dotted lines in the diagram represent hydrogen bonded cross links between the two cellulose chains. Hydrogen bonding occurs where the chains are sufficiently close; it is rather limited in the readily accessible region. Diagram B illustrates what can happen when the fiber is dried. In the dry collapsed fiber the cellulose chains, especially in the accessible region, become closer, permitting a higher degree of hydrogen bonding and a higher degree of wrinkle recovery in a fabric. When a fiber is wet in water, it swells about 20%. Diagram C illustrates the two cellulose chains in a wet fiber. The water not only enters the highly accessible regions but also the somewhat less accessible regions, breaking many of the hydrogen bonds and reducing wrinkle recovery in a fabric.

Now, consider what happens to the cellulose chains when they are cross-linked through covalent bonds while in a relatively collapsed condition. This is the condition existing when cotton is finished by the pad, dry, and cure process, as with the N-methylol type finishing agents in current use for producing wash-and-wear goods. Although the fiber is greatly swelled initially and many hydrogen bonds are disrupted by the aqueous media, much of the water is distilled out by the drying and curing operations before the latent acid catalyst becomes effective in promoting cross-linking. Many of the hydrogen bonds are re-established when most of the water is driven out of the fibers. This takes place before a significant amount of primary valence cross-linking because extensive cross-linking restricts collapsing of the microstructures. Diagram A of Figure 16 illustrates the location of covalent cross links (solid links) occurring between the two cellulose chains. These cross links occur mostly in the highly accessible region but to a lesser extent in the originally hydrogen-bonded regions. The experimental data support this idea. The cross-linked fiber is less dense than the original fiber, yet less accessible to the direct dye molecule. This implies that the original accessible regions have been made less accessible. But to account for reduced dry density or an over-all increase in volume, the original dense or hydrogen-bonded regions must have become less dense. The experimental evidence indicates that primary valence cross links can account for the reduced density. The new covalent-bond cross links in combination with the hydrogen-bond cross links restrict slippage of the microstructures and thus provide dry wrinkle recovery. When dry or when wet, the covalent-bond cross links stabilize the fiber and restrict swelling, as shown in Diagram B of Figure 16. Fabrics containing cross-linked molecules, as represented in Diagrams A and B, are characterized by wet and dry wrinkle recovery and a low degree of swellability, as

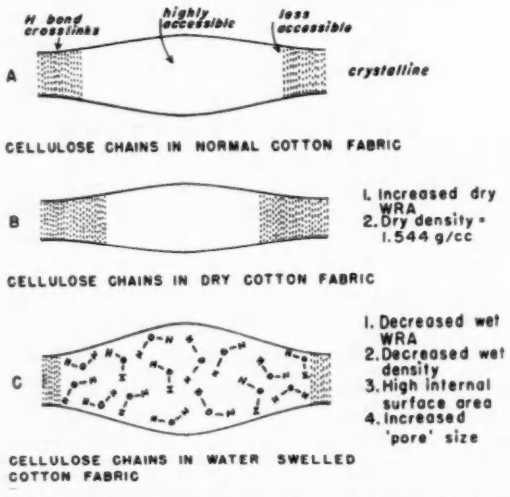

Fig. 15. Hydrogen bonded cross links of cellulose chains in cotton fabric.

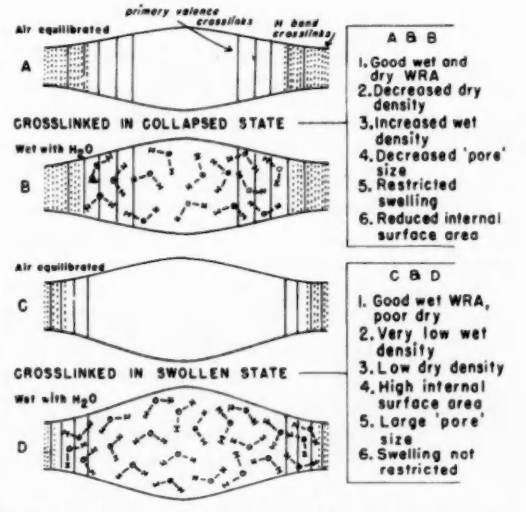

Fig. 16. Bonding of cellulose chains in wrinkle-resistant cotton fabric.

determined by wet density, low moisture regain, low water of imbibition, and decreased dye receptivity.

Cotton fabrics cross-linked while in a highly swollen state were shown above to be substantially different from those cross-linked in a relatively collapsed condition. Thus, to account for these different properties, the cross links between the cellulose chains are in different locations. In this case, water and the cross-linking agent penetrate into the hydrogen-bonded region, disrupt many of the hydrogen bonds between the cellulose chains, and cross link the cellulose. The cross links occur mainly in the originally hydrogen-bonded regions, as shown in Diagram D. The readily accessible regions were swelled by the water to such an extent that the length of the cross-linking agent could no longer span the distance between the two cellulose chains. Therefore, there must be much less cross-linking in these regions. When the reaction is completed and the fiber is washed and dried, the two cellulose molecules may be represented as in Diagram C. Here the covalent-bond cross links have mostly replaced hydrogen-bond cross links so that the cross-linked region, with respect to the two chains, is not changed much; an increase in dry WRA would not be expected under these conditions. However, an increase in wet WRA could be expected, since water could no longer destroy the cross links that were originally only hydrogen bonded. But water could reswell the fiber, as in Diagram D, so that distortion from external forces would be resisted. Fabrics cross-linked in the highly swollen state are characterized by wet, but little or no dry, wrinkle recovery, low wet density, high moisture regain, increased dye receptivity, and high water of imbibition.

The diagrams used above are no doubt highly oversimplified representations of the facts, for it is fully recognized that the cotton fiber is a three-dimensional network. Yet they serve to illustrate the importance of primary valence cross links, hydrogen-bonded cross links, and location of cross links.

It should be remembered that the diagrams represent the extremes and that there is a gradual transition from one extreme to the other, as shown by the properties of the fabrics treated under different states of fiber swelling. Although the diagrams have illustrated the cross-linking or binding of two cellulose chains, it is readily apparent that binding of microfibrils and even layers of the secondary cell wall are obtained when the cellulose molecules involved are in different microfibrils or layers.

Summary

An examination of the wet and dry wrinkle recovery and the wet and dry densities of fabric finished with known types of wash-and-wear finishing agents was made. All of the finishes applied by the pad, dry, and cure process exhibited good wet and dry wrinkle recovery. The finishes applied by reaction in aqueous solution produced fabrics with an increase in only wet wrinkle resistance and these fabrics had a more open structure. Examination of the above fabrics led to a study of fabrics which had been cross-linked under various states of fiber swelling. Print cloth was cross-linked with formaldehyde, using hydrochloric acid as catalyst in systems with varying amounts of water and acetic acid. The aqueous systems provided considerable swelling of the cotton fiber before and during cross-linking, while the systems containing large amounts of acetic acid provided relatively little swelling of the fibers.

The formaldehyde cross-linked fabrics were studied with respect to wet and dry wrinkle recovery, wet and dry density, dyeability with a direct dye, moisture regain, water of imbibition, and wash-and-wear properties. The state of the fiber swelling at the time of cross-linking had a tremendous influence on fiber structure and on the resulting physical properties of fabric made from the fibers. All of the fabric properties studied and listed above were altered according to the state of fiber swelling at the time of cross-linking; no doubt many other properties not studied here, such as tear and tensile strength, abrasion resistance, permanent set, and dimensional stability, are affected by the amount of fiber swelling. A high degree of fiber swelling resulted in fabric with wet but little or no increase in dry wrinkle recovery and good drip-dry properties. Relatively little swelling resulted in fabric with good wet and dry wrinkle recovery and also good wash-and-wear properties when either drip dried, line dried, or tumble dried.

A mechanism, diagramatically illustrated, is described which proposes an explanation of wet and dry wrinkle recovery in cotton fabrics. The mechanism embodies three important factors: cross-linking through primary valence cross links, cross-linking through secondary valence bonds, and the location of the cross links. Experimental evidence is presented in support of the mechanism.

Acknowledgments

The authors wish to express their appreciation to Mrs. Vidabelle O. Cirino and James A. Harris for the many formaldehyde determinations.

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The Cross-Linking of Cotton Cellulose with Quaternary Ammonium Derivatives of Bis Chloromethyl Ethers[1]

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Introduction

In 1948, Cameron and Morton [2] suggested that certain polyfunctional reagents enhance the crease recovery of cellulosic fabrics by cross-linking adjacent cellulose chains. Direct experimental proof of this hypothesis has not been obtained even today, and some investigators still maintain that factors other than cross-linking are important, or even essential, for increasing the elastic recovery of cellulose fibers and the crease recovery of cellulosic fabrics. However, progress in the theoretical knowledge of polymer chemistry and the accumulation of valid (even though indirect) experimental evidence have favored the cross-linking hypothesis heavily, and the postulate that the cross-linking of cellulose chains is essential for imparting a satisfactory level of crease recovery to cellulosic fabrics is now widely accepted as fact. In the cross-linking of cellulosic fabrics, the following factors are known to have a profound effect on the physico-mechanical properties of the cross-linked polymer:

1. The properties of the linear cellulose polymer (for example, accessibility, degree of polymerization, etc.).
2. The reaction conditions required.
3. The extent of the cross-linking reaction.
4. The structure and distribution of the cross links formed.

A meaningful quantitative relationship between even one of these factors and the crease recovery of a cross-linked cellulosic fabric would be truly important for the understanding of the mechanism by

[1] Presented at the 8th Chemical Finishing Conference of the National Cotton Council of America, October 7, 1959.

which the crease recovery, tensile strength, and other mechanical properties are altered when the cellulose chains are linked to form a three-dimensional network.

Such quantitative relationships are exceedingly difficult to develop—and indeed are not available to us. In discussing the relation between network elasticity and degree of cross-linking for a vulcanized rubber, Treloar [18] states that "Attempts to verify a theoretical relation between modulus and degree of cross-linking have met with considerable difficulty because of the difficulty of finding a method of introducing a precisely determined number of cross-linkages."

This statement is essentially applicable to the present status of the theory of cellulose cross-linking. It is the purpose of this paper to report some progress in developing a quantitative correlation between the number of cross links introduced into a cellulosic fabric and the resulting changes in fabric properties.

In order to make such a correlation possible, it is essential that the cross-linking reaction should fulfill the following requirements.

1. It should involve the use of a polyfunctional cross-linking agent capable of forming stable chemical bonds with the hydroxyl groups of the cellulose molecule under conditions which do not adversely affect the fiber. The simplest case is that of a symmetrical bifunctional reagent.

2. The cross-linking reagent should not be capable of polymerization or self-condensation under the prevailing reaction conditions. In other words, resin deposition and formation of polymeric cross links should be avoided.

3. The functional groups of the cross-linking agent should react completely, so that formation of monomeric side chains is avoided. This condition is more easily met with a reagent where all functional groups have equal reactivity.

4. The cross link formed should not contain functional groups, such as hydroxyl groups, which can become reaction sites and lead to the formation of polymeric side chains in a graft polymerization reaction.

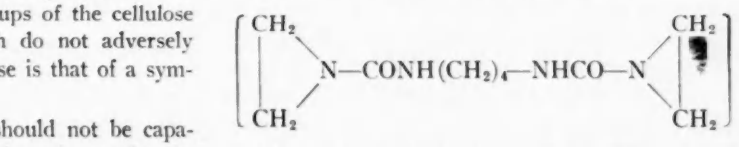
5. Decomposition of the cross-linking reagent should preferably not take place under the prevailing reaction conditions. If decomposition does occur, it should result in the formation of byproducts which are not capable of reaction with cellulose and can be readily removed.

6. Similarly, the cross-linking agent should not combine with the reaction medium (usually water) at an appreciable rate. If it does, it should form unreactive byproducts which can be readily removed.

7. Intramolecular cross-linking (cyclization) should be insignificant under prevailing reaction conditions.

It is apparent that the cross-linking agents which are commonly used in creaseproofing finishes do not fulfill the requirements listed. The thermosetting resins, the polyepoxides, polyacetals, and polyfunctional ethylene imine derivatives all exhibit (to varying degrees) a tendency to polymerize under the conditions required for reacting them with cellulose hydroxyl groups; the efficiency of their reaction with cellulose is generally of the order of 50–70%, and we must conclude that side reactions play an important role. Quantitative analyses of some of these reactions and reaction products have been attempted by various investigators, but they required some unwarranted assumptions which impaired the significance of the resulting generalizations.

Recently, Tokita and Kanamaru [17] investigated the cross-linking of viscose rayon filaments with tetramethylene diisocyanate ($OCN-(CH_2)_4-NCO$) and with tetramethylene bis ethylene urea,



(TBU) and calculated the average number (Z) of glucose residues between the junction points of the cross-linked molecule from the nitrogen content of the cross-linked fiber. In the case of TBU, the assumption was made that four atoms of nitrogen were equivalent to one cross link and thus that no polymerization of the reagent or side chain formation took place.

By further assuming that the degree of crystallinity was not altered during the cross-linking reaction, and that cross-linking took place entirely between cellulose molecules in noncrystalline regions, they derived the following relationship

$$Z^* = Z \times \left(1 - \frac{\text{degree of crystallinity}}{100}\right)$$

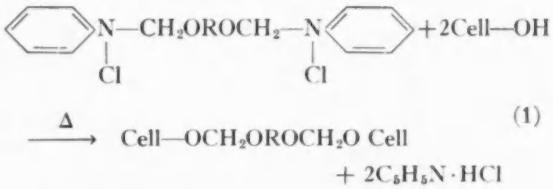
where Z^* represents the average number of glucose residues between junction points in the noncrystalline regions. For a completely amorphous cellulose, $Z^* = Z$. For cotton, which may be assumed to be about 80% crystalline, $Z^* = Z/5$.

These relationships imply the conclusion that for a given value of Z, Z^* is at least twice as large for ordinary textile rayon as it is for cotton, where accessibility is lower.

The values of Z and Z^* which Tokita and Kanamaru calculated for viscose rayon cross-linked with TBU were correlated with the dynamic properties of the fiber. No attempt was made to establish the efficiency of the cross-linking reaction in terms of side reactions or byproducts, and all treatments involved relatively low degrees of cross-linking ($Z^* = 7$ to 24).

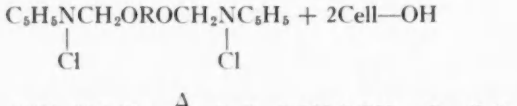
The Reaction of Quaternary Ammonium Derivatives of Bis Chloromethyl Ethers with Cellulose

In the search for a cross-linking reaction which would fulfill the requirements outlined earlier, and possibly allow a meaningful correlation of Z and Z^* with the crease recovery of a cross-linked cotton fabric, a study of the reaction of bis pyridinium salts of bis chloromethyl ethers of aliphatic glycols with cotton cellulose was carried out in this laboratory. This reaction can be formulated as follows:



$$\xrightarrow{\Delta} \text{Cell—OCH}_2\text{OROCH}_2\text{O Cell} + 2\text{C}_5\text{H}_5\text{N}\cdot\text{HCl} \quad (1)$$

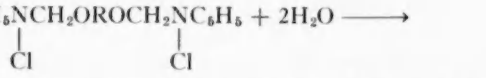
It is apparent that pyridine hydrochloride is a byproduct of the reaction. Since pyridine hydrochloride is a strongly acidic material which damages cellulose on heating, a suitable buffer (e.g., sodium acetate) must be present. The reaction then becomes



$$+ 2\text{CH}_3\text{COONa} \xrightarrow{\Delta} \text{Cell—OCH}_2\text{RCH}_2\text{—O—Cell} + 2\text{NaCl} + 2\text{C}_5\text{H}_5\text{N} + 2\text{CH}_3\text{COOH} \quad (2)$$

Pyridine and acetic acid are removed by evaporation.

The choice and amount of buffer are important, and will be discussed in detail later. If, however, the byproduct pyridine hydrochloride can be neutralized and removed without difficulty, the following side reactions are possible in addition to the desired Reaction (1). The bis pyridinium compound may decompose as follows (in presence of water):



$$2\text{C}_5\text{H}_5\text{N}\cdot\text{HCl} + 2\text{HCHO} + \text{HOROH} \quad (3)$$

In this case, the formaldehyde formed may react with cellulose.

$$2\text{Cell—OH} + \text{CH}_2\text{O} \longrightarrow \text{Cell—OCH}_2\text{—O—Cell} \quad (4)$$

Also, it may recombine with the glycol and form polyformals:

$$X(\text{CH}_2\text{O}) + X(\text{HOROH}) \xrightarrow{\text{H}^+} [\text{OCH}_2\text{OR}]_X + X(\text{H}_2\text{O}) \quad (5)$$

The formation of polyformals may also proceed as follows:

$$2\text{CH}_2\text{O} + \text{HOROH} \longrightarrow \text{HOCH}_2\text{OROCH}_2\text{OH} \quad (6)$$

and

$$X(\text{HOCH}_2\text{OROCH}_2\text{OH}) \longrightarrow [\text{OCH}_2\text{OROCH}_2]_X + X(\text{H}_2\text{O}) \quad (7)$$

The polyformals thus formed may react with cellulose by fragmentation and trans-acetalization, leading to methylene and polyformal cross links:

$$\begin{aligned} &\text{Cell—O—CH}_2\text{—O—Cell} \\ &\text{Cell—[OCH}_2\text{OR]}_X\text{—OCH}_2\text{—O—Cell} \\ &\text{Cell—[OCH}_2\text{OROCH}_2\text{]}_X\text{—OCH}_2\text{—O—Cell} \end{aligned} \quad (8)$$

While all these reactions lead to the formation of cross-linked cellulose, it is apparent that, after the soluble byproducts are removed by washing, the theoretical weight increase (calculated for a given amount of reagent) can be obtained only if the cross-linking reaction takes place as shown in Reaction (1). If the reaction takes place according to Equations (3) and (4), the weight gain is greatly reduced by the loss of the group —O—R—O—. If the cross-links formed are those shown in (8), (postulating the occurrence of Reactions (3), (4), (5), (6), and (7)), the observed weight gain must also be lower than calculated, due to the decomposition (3) and to the low efficiency of the trans-acetalization reaction be-

tween polyformals and cellulose, known to be of the order of 50% [7, 8, 9].

The formation of side chains by reactions similar to those yielding the cross links shown in (8) is subject to the same considerations and is also likely to result in weight gains lower than calculated for a given amount of reagent.

The investigation reported presently showed that, under specific conditions (and under specific conditions only), the reaction proceeded quantitatively, seemingly free of undesirable side reactions; the weight gains obtained in the reaction between the bis pyridinium salts and cotton fabric checked very well with the values calculated for Reaction (1). If the extent of the side reactions can truly be minimized by a suitable choice of conditions, as indicated by these findings, then the number of cross links formed per anhydroglucose residue can be derived from the weight gain observed and the molecular weight of the cross link formed. Furthermore, the size, structure, and rigidity of the cross link can be varied for a given number of cross links. Thus it may be possible to derive some significant relationships between the number and structure of the cross links introduced and the physical properties of the cross-linked fabric by the use of this reaction.

While the reaction of bis pyridinium salts of bis chloromethyl ethers with cellulose has been reported in the literature on several occasions [1, 4, 5, 6, 13, 14, 16, 20], no quantitative study of the reaction was attempted previously, and in the light of our experimental results it appears that the reaction conditions used by previous investigators did not avoid the decomposition of the cross-linking agents, formation of formaldehyde, and side reactions.

Experimental

Preparation

The preparation of bis- and poly-chloromethyl ethers from aliphatic glycols and polyols is known, and many such compounds are described in the literature [3, 10, 11, 12, 15]. The preparation is carried out from the glycol, formaldehyde, and hydrochloric acid at low temperature, and the products are purified by vacuum distillation. Some of the publications also describe the conversion of the bis- and poly-chloromethyl ethers to the corresponding quaternary ammonium compounds by reaction with a tertiary base such as pyridine. It is apparent that structural variations of cross-linking agents of this type can be achieved with relative ease, simply by varying the structure of the glycol employed in the preparation of the halogenated derivative. Table I shows some of the compounds which have been prepared in our laboratory.

The products are white crystalline solids which readily absorb moisture from the surrounding medium (atmosphere or solvent). Some of the compounds are so hygroscopic that they cannot be isolated in crystalline form by common laboratory techniques; purification and characterization of the compounds is difficult for this reason.

The presence of impurities (mainly glycol, formaldehyde, and pyridine hydrochloride) in the compounds studied was found to have a significant effect on the course of their reaction with cellulose; a suitable analytical method was developed for establishing the actual content of quaternary ammonium compound in each preparation. This consisted of an electrometric titration for hydrogen ion which, coupled with an argentometric chloride analysis, established in each case the composition of the materials. By this procedure, the initial purity and the extent of decomposition of the compounds on aging in aqueous solution and in solid form was determined. The stability of the compounds was found to vary somewhat with the structure. Generally speaking, dilute aqueous solutions of the products are stable at room temperature for a period of 24 hr. or more. The rate of decomposition and liberation of acid is greatly accelerated by increasing the temperature and/or concentration of the aqueous solution. The solid compounds are stable at room temperature if stored in a dry atmosphere, but decompose when exposed to atmospheric moisture for a prolonged period.

The four compounds listed in Table II were selected for more extensive investigation of their reaction with cellulose.

Reaction

The reaction of the compounds with cellulose was carried out by the following general procedure. Swatches of 80 × 80 cotton print cloth (bleached and desized) were conditioned at 65% RH and 70° F., weighed on an analytical balance, padded to 80% wet pickup (40 lb. pressure on a laboratory padder) with an aqueous solution containing the reagent and buffer salt, dried on frames at 100–120° F., cured on the frames, washed thoroughly at 110–120° F. with nonionic detergent, dried, conditioned at 65% RH

and 70° F., and weighed. Control swatches padded with water and with a solution containing buffer salt only were included in all experiments as an aid to establishing the time at which conditioning equilibrium was reached and for comparison of physical properties. From the observed weight gain, the percentage yield, (observed wt. gain/calculated wt. gain) × 100, could be calculated.

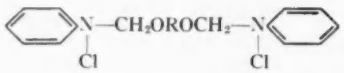
It was established that the moisture regain of the cross-linked fabric at 65% RH did not differ significantly from the moisture regain of the control samples; therefore no regain correction was necessary in the calculation of experimental weight gains.

The results of this regain experiment for fabrics cross-linked with the EG compound under optimum conditions are summarized in Table III.

It is apparent that cross-linking does not affect the moisture regain of cotton under the conditions studied.

After the weight at 65% RH was determined, the treated samples and the controls were tested for crease recovery (Monsanto method), tensile strength

TABLE I



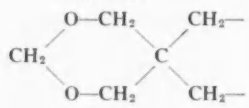
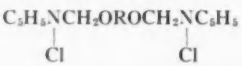
R =	% Cl Calc'd	% Cl Found	Remarks
$-CH_2CH_2-$	22.4	22.0	—
$-CH_2CH_2OCH_2CH_2-$	19.6	19.3	—
$-CH_2CH_2OCH_2CH_2OCH_2CH_2-$	17.5	—	Could not be crystallized
$-CH(CH_3)-CH_2-$	21.4	21.2	—
$-CH_2CH_2CH(CH_3)-CH_2CH_2-$	19.2	—	Could not be crystallized
$-CH_2CH_2CH_2CH_2-$	20.6	18.0	Contains solvent of crystallization
$-CH_2CH_2CH_2CH_2CH_2-$	19.8	19.2	—
$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$	16.5	16.0	—
$-CH_2CH=CHCH_2-$	20.6	—	Could not be crystallized
$-CH_2CH(Br)-CH(Br)-CH_2-$	14.1	—	Decomposes rapidly on standing
$-CH_2CH(Cl)-CH(Cl)-CH_2-$	34.2 (Total)	—	Decomposes slowly on standing
	17.6	17.2	—

TABLE II



R =	Glycol used	Code name	M. wt of cross link formed	Chain length of cross link formed
$-CH_2CH_2-$	Ethylene glycol	EG	88	6
$-CH_2CH_2OCH_2CH_2-$	Diethylene glycol	DEG	132	9
$-CH_2CH_2CH_2CH_2CH_2-$	1,5-Pentane diol	PD 1,5	130	9
$-CH_2(CH_2)_8CH_2-$	1,10-Decane diol	DD 1,10	200	14

TABLE III

EG compound conc., eq./l.	Weight gain, % Calculated	Found	Moisture regain at 65% RH, 70° F., %
1.26	4.5	4.6	8.6
1.26	4.5	4.4	8.5
0.63	2.25	2.2	8.4
None (control)	0	0	8.7

(strip method), and tear strength (tongue method) initially and after laundering at 140° F. As expected, the chemical bond formed in the cross-linking reaction (—OCH_2OROCH_2O—) was found to be substantially permanent to laundering under normal conditions.

Reaction Conditions

The following variables were found to have a significant effect on the course of the cross-linking reaction and on the physical properties of the cross-linked fabrics.

1. The purity of the compound used.
2. The choice of buffer salt and the amount used.
3. The time and temperature of curing.

The compounds selected for this study contained a minimum of 92% quaternary ammonium compound by analysis. It was also shown experimentally that an optimum range of Condition 2 exists for each value of 3 and that the reverse is also true. The experiments reported here were carried out within specific ranges of Conditions 2 and 3, the choice of conditions being dictated by preliminary screening experiments and by some general considerations of a practical nature. The pH of the bath was controlled in all applications by the use of acetic acid or sodium bicarbonate as needed, but the extensive pH changes which take place on the fabric during the reaction were not determined or controlled. Sodium acetate was found to be a satisfactory buffer salt for the reaction. For a given set of curing conditions, the optimum ratio (in equivalents) of sodium acetate to bis quaternary ammonium compound must be found. If the amount is too high, the reaction is exceedingly slow. If the amount is too low, the cross-linking reaction takes place rapidly, but the highly acidic conditions prevailing cause decomposition of the cross links formed (formation of formaldehyde) and severe damage to the fabric. Figure 1 shows the percent yield obtained by curing 3 min. at 300° F. with varying amounts of sodium acetate buffer; this relationship is further illustrated in Figure 2, where the reaction rates with 80% (Curve I) and 100% (Curve II) of the calculated amount of sodium acetate are compared. The effect of treating with solutions of pyridine hydrochloride/sodium acetate only on the tensile strength of the fabric is shown in Figure 3; in absence of a cross-linking reagent, there was no change in the crease recovery of the fabric, but a considerable loss in tensile strength was observed even when a stoichiometric amount of sodium acetate was used in combination with the pyridine hydrochloride. It is

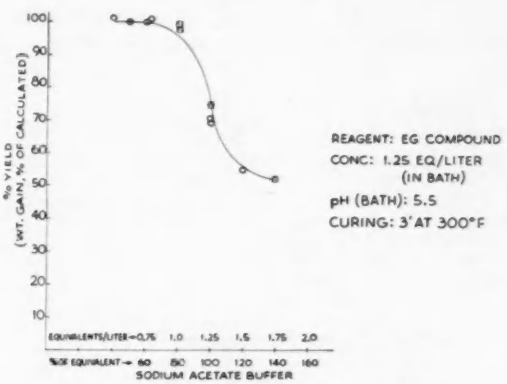


Fig. 1. Amount of buffer vs. percent yield.

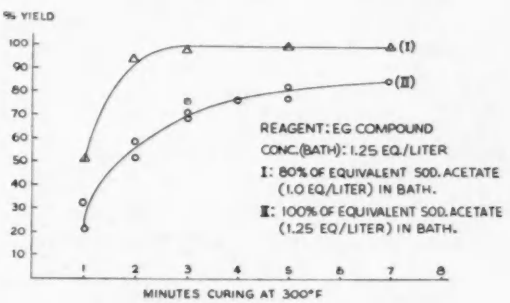

% YIELD
REAGENT: EG COMPOUND
CONC.(BATH): 1.25 EQ./LITER
I: 80% OF EQUIVALENT SOD. ACETATE (1.0 EQ./LITER) IN BATH.
II: 100% OF EQUIVALENT SOD. ACETATE (1.25 EQ/LITER) IN BATH.
MINUTES CURING AT 300°F

Fig. 2. Curing time vs. percent yield.

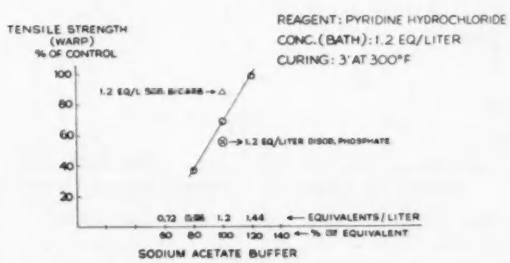


Fig. 3.

known [8] that fiber damage and losses in tensile strength on heating cotton with acid-forming substances are greater in absence of cross-linking agents than in their presence; it appears, therefore, very difficult to separate the effect of byproduct salts and reaction medium from the over-all effect of the cross-linking reaction on tensile strength. This difficulty does not apply to the correlation of cross-linking with crease recovery.

For a given concentration of bis pyridinium compound and buffer salt, the weight gain reaches a maximum, then decreases with increasing severity of curing conditions. This decrease in weight gain is not accompanied by a decrease in crease recovery, but is accompanied by losses in tensile and tear strength. Prolonged heating, as in the case of insufficient buffer, appears to cause decomposition, formation of formaldehyde, and undesirable side reactions. Some of these facts are illustrated by the tensile strength–crease recovery curves shown in Figure 4.

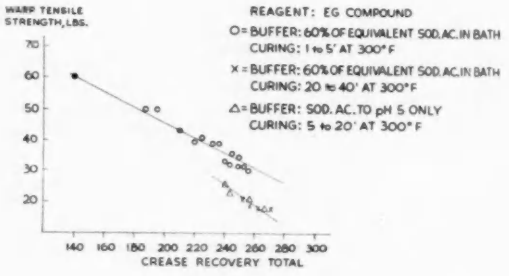

WARP TENSILE STRENGTH, LBS.
REAGENT: EG COMPOUND
O = BUFFER: 60% OF EQUIVALENT SOD. AC. IN BATH CURING: 1 to 5' AT 300° F
X = BUFFER: 60% OF EQUIVALENT SOD. AC. IN BATH CURING: 20 to 40' AT 300° F
Δ = BUFFER: SOD. AC. TO pH 5 ONLY CURING: 5 to 20' AT 300° F
CREASE RECOVERY TOTAL

Fig. 4.

On the basis of these findings, the four compounds listed in Table II were reacted with cellulose under conditions which would essentially avoid side reactions; the physical properties of the cross-linked fabrics thus obtained were evaluated. The yields obtained are shown in Figure 5. The agreement between calculated and observed weight gain is excellent for the four compounds throughout the concentration range studied.

Figure 6 illustrates the results obtained with the EG compound by using 60% of the calculated amount of sodium acetate in the bath and varying the curing conditions and concentration as indicated. Similar results were obtained when the other compounds studied were applied under the same conditions.

Under controlled conditions, the reaction of bis pyridinium salts of bis chloromethyl ethers prepared from aliphatic glycols may provide a tool for introducing a predetermined number of cross links into the cellulose molecule.

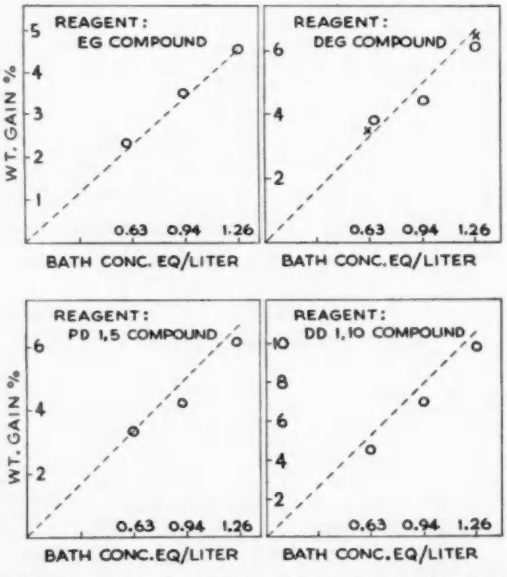


Fig. 5. Experimental points obtained with 60% of the equivalent amount of sodium acetate, curing 3 min. at 300° F., pH 5–6. - - - indicates the calculated weight gain for bath; fabric and procedure as described.

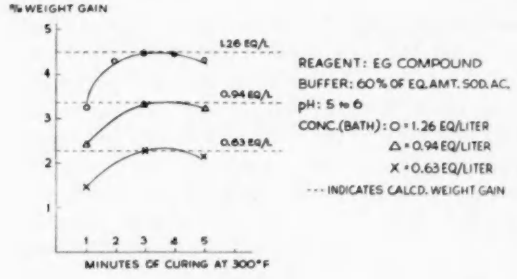

% WEIGHT GAIN
1.26 EQ/L.
0.94 EQ/L.
0.63 EQ/L.
REAGENT: EG COMPOUND
BUFFER: 60% OF EQ. AMT. SOD. AC.
pH: 5 to 6
CONC. (BATH): O = 1.26 EQ/LITER
Δ = 0.94 EQ/LITER
X = 0.63 EQ/LITER
--- INDICATES CALCD. WEIGHT GAIN
MINUTES OF CURING AT 300° F

Fig. 6.

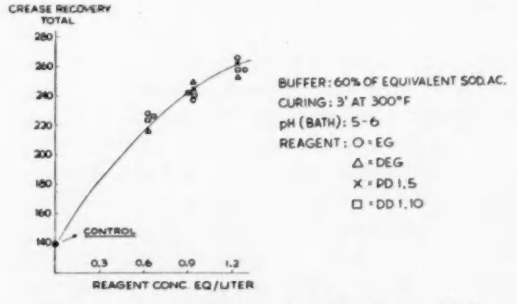


Fig. 7. Crease recovery vs. equivalents applied.

Properties of Cross-Linked Fabrics

Figure 7 illustrates the relationship between the crease recovery and the concentration (in equivalents per liter) of the cross-linking agent in the impregnating solution at constant buffering and curing conditions. The application conditions selected were those which resulted in near-quantitative weight gains, the actual weight gain depending, of course, on the molecular weight of the cross link formed and varying by a factor of 2.3 from the lowest, EG:

$$—CH_2OCH_2CH_2O—CH_2—$$ m. wt. 88

to the highest, DD 1,10:

$$—CH_2OCH_2(CH_2)_8CH_2OCH_2—$$ m. wt. 200

among the compounds studied.

It is apparent from Figure 7 that equivalent concentrations of cross-linking agents give equal crease recoveries (within the limits of experimental error). This suggests strongly that the crease recovery is primarily a function of the number of cross links formed.

A similar relationship between warp tensile strength and concentration of cross-linking agent (in equivalents per liter) is shown in Figure 8. The effect of the cross-linking agents on tensile strength also appears to be independent of the molecular weight (and weight add-on) of the reagents, since equivalent concentrations of cross-linking agents give comparable losses in tensile strength. This conclusion must be viewed with caution, however: while the byproduct salts formed during reaction do not affect the crease recovery of the fabric, they do affect the tensile strength (see Figure 3), and the curve shown in Figure 8 actually represents the composite effect on tensile strength of the cross-linking reaction and of heating in presence of the byproduct salts.

The correlation of crease recovery with warp tensile strength is shown in Figure 9 for samples treated with four different cross-linking agents over a relatively broad range of application conditions. In the range studied, there is no indication that structural differences in the cross link have a significant effect on the tensile strength or crease recovery of the cross-linked fabric.

A study of the values obtained for tear strength on the cross-linked fabrics, however, indicates that this property may be dependent on cross link structure. Table IV summarizes some pertinent data.

The available experimental results are not sufficient to allow generalizations, but the excellent tear strength retained with cross links containing the long decamethylene chain appears consistent with the theory of cross link elasticity as discussed, for example, by Van Bochove [19].

Discussion

The requirements which have been outlined for a quantitative cross-linking reaction are as follows:

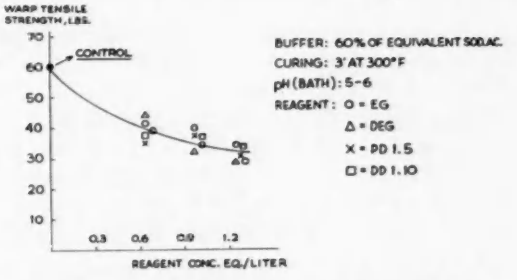


Fig. 8. Tensile strength vs. equivalents applied.

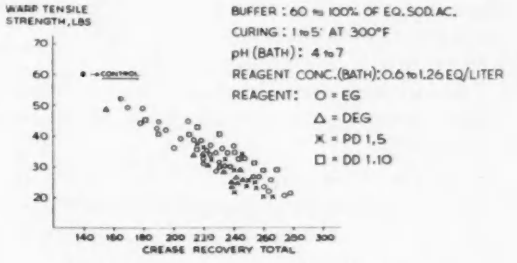


Fig. 9. Crease recovery vs. tensile strength.

TABLE IV

Reagent	Eq./l.	Weight add-on: Found	Weight add-on: Calculated	Crease recovery, total	Warp tear, lb.	Warp tensile, lb.
E	1.26	4.5	4.5	253	1.0	32
DEG	1.26	6.3	6.6	257	0.8	30
PD 1,5	1.26	6.3	6.6	260	0.9	31
DD 1,10	1.26	9.9	10.2	255	1.6	35
None	—	—	—	140	1.9	60

TABLE V

Eq./l. in solution (EG compound)	0.63	0.94	1.26	1.75
Z (Approx.)	12	8	6	Calc'd 4 Found 5
Z^* (80% Crystallinity)	2.4	1.6	1.2	Calc'd 0.8 Found 1.0
Crease recovery, total	220	240	260	270

1. Cross-linking reagent capable of forming stable chemical bonds with cellulose OH groups.
2. No formation of polymeric cross links and no resin deposition.
3. No side chain formation.
4. No graft polymerization.
5. No decomposition of the cross-linking agent.
6. No reaction of the cross-linking agent with the medium (water).
7. No intramolecular cross-linking (cyclization).

It appears that, under carefully controlled conditions, the reaction of bis pyridinium salts derived from bis chloromethyl ethers of aliphatic glycols is capable of fulfilling Requirements 1 through 6.

Values of Z and Z^* (as defined by Tokita and Kanamaru [17]) may be calculated for cotton fabric cross-linked with the pyridinium salts of bis chloromethyl ethers by the use of the following equation:

$$\frac{\%\text{ wt. gain}}{100} = \frac{\frac{1}{2}\text{ cross link m. wt.}}{162\ Z\text{ cross link m. wt.}}$$

where Z = average number of glucose residues between junctions in the cross-linked molecule and 162 = m. wt. of anhydroglucose unit.

Table V summarizes the values obtained from the experimental weight gains (except where otherwise indicated).

It is interesting to note that the experimental weight gain did not reach the calculated value in the case of a reagent concentration of 1.75 eq./l. and that the maximum observed weight gain coincides with $Z^* = 1$. Figure 10 shows graphically the values given in Table V and suggests that a linear relationship may exist between Z (or Z^*) and crease recovery in the range studied. Also it appears difficult to obtain a Z^* smaller than 1, and a value of 270 for crease recovery may be the maximum which can be reached on the specific cotton fabric employed, by the sole use of the cross-linking reaction discussed here, under the conditions investigated.

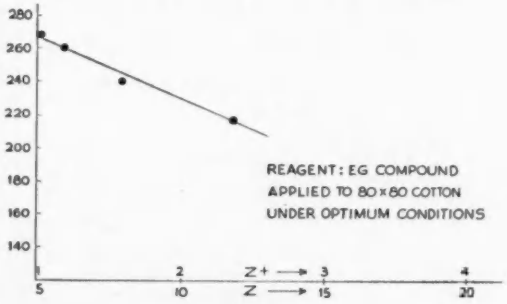


Fig. 10.

Summary and Conclusions

The cross-linking of cellulose with bis quaternary ammonium compounds derived from bis chloromethyl ethers of aliphatic glycols has been studied. This reaction can be carried out under conditions which minimize or avoid side reactions and may be useful for the quantitative study of cellulose cross-linking.

By varying the structure of the aliphatic glycol employed in the preparation of the compounds, the effect of cross link structure on the properties of the cross-linked polymer may be studied; specifically, the effect of cross link length and rigidity and of hetero-atoms and bulk may be investigated, and conclusions may be reached concerning the penetration and reactivity of molecules of varying size and shape.

The reaction might also be employed for introducing specific atoms (such as halogens) into the cellulose molecule. By extending the study to compounds prepared from alcohols and polyols, the functionality of the reagent may be varied. A comparative study of monofunctional compounds has been attempted, employing the pyridinium salts of the chloromethyl ethers prepared from n-butanol, n-octanol, and n-decanol. Unfortunately, however, the monofunctional compounds appear to decompose more readily than bifunctional compounds, and optimum conditions for their reaction with cellulose have not yet been established. A study of mono- and polyfunctional compounds is in progress.

The reactivity of the quaternary ammonium compounds may also be modified by varying the tertiary base employed in their preparation. Some of the results reported recently by Rath [14] are of interest in this connection.

Acknowledgments

The author wishes to acknowledge gratefully the help of Bernard Chidiac and Carl Of in carrying out

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The Mechanism of Resin Deposition in Cotton[1]

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Abstract

A theoretical discussion of the mechanism leading to resin deposition inside cotton fibers is given, and the hypothesis presented is substantiated by experimental results.

It is demonstrated that expression of excess precondensate from fabrics in the padding process does not play a decisive role. A simple immersion process without squeezing, or spraying with the precondensate, is sufficient to obtain the desired crease resistance and swelling reduction.

Roll pressure affects the results of the treatment only insofar as it determines the amount of add-on and the uniformity of the finishing effect. Resin applied by immersion or by spraying is also deposited inside fibers, and therefore the result is nearly the same as that obtained by padding.

Resin deposition and location inside cotton fibers, achieved by the various application methods, is demonstrated by means of an especially developed staining test.

Introduction

Although the skill we have now acquired in the application of synthetic resins is quite sufficient to obtain preplanned effects, the factors promoting the process of resin deposition in the fibers are not fully clarified. For this reason it appeared worthwhile to investigate one aspect of this complex problem on a broad experimental basis.

The question we singled out for study was as follows: does the method of application of the precondensate determine the deposition of synthetic resins and thus also the effects attainable?

Although conclusions may be drawn from this investigation as to the processes leading to resin deposition, it should be understood that, for the time being,

[1] Presented at the Chemical Finishing Conference of the National Cotton Council of America, Washington, D. C., October 7, 1959.

they can be taken only as hints as to what presumably happens during such processes.

The selected methods of application deviate from those of standard practice, and therefore are not of practical use. In fact, they represent only a few variations within the experimental framework of the present investigation, although it may be added that the possibility of practical application of one of these methods is currently being examined.

Discussion

The Function of Pressure

In the process of imparting crease and swelling resistance by resin deposition it has been postulated that the step of expressing precondensate from capillaries between fibers is necessary to attain the highest possible deposition within fibers. The pressure in padding is thought to have the function of "pressing in" the precondensate solution to the fiber interior. This is the reason for which a maximum degree of squeezing is recommended.

The questions arise whether during impregnation the fibers in a cotton fabric are actually capable of absorbing the required quantity of precondensate and whether it is possible in the padding operation to squeeze out the entire liquid between the fibers and to retain only the solution which has penetrated within the fibers.

After equilibrium has been established, the water content of cotton fiber swollen in water, that is, the quantity of water contained exclusively inside the fiber, is approximately 30%. This figure also denotes the capacity of a nonmercerized cotton fiber to absorb water or an aqueous solution of similar density. (For mercerized cotton the value is somewhat higher.)

In the case of nonmercerized cotton fabrics, it follows that at a wet pick-up of 100%, approximately 30% of the precondensate will be within fibers after a certain period of impregnation, while 70% will be in the capillaries between fibers and also between yarns. The absorbing capacity of fibers cannot be increased by pressure. The concentration of precondensate within fibers can be increased only by diffusion due to some effects of the drying process. In this manner, under suitable conditions, a major portion of the precondensate can be deposited within fibers.

It is impossible to remove by pressure all of the liquid located between fibers, that is the capillary fluid, even if the wet pick-up is considerably below 100%. Fabrics leaving the squeezing rolls are highly absorbent and will therefore tend to reabsorb any available liquid into the capillaries between the fibers. Under these circumstances the amount of liquid which can be removed by pressure from spaces between fibers is rather limited. Effects of centrifuging are, again,

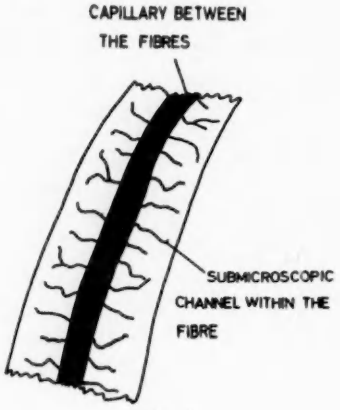


Fig. 1

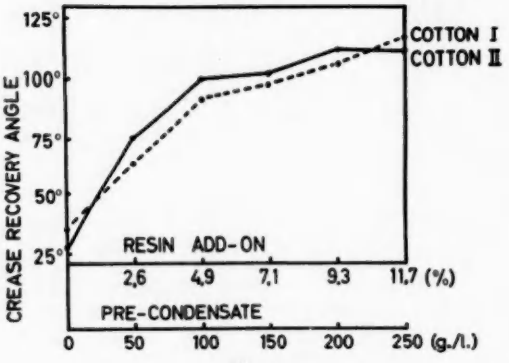


Fig. 2

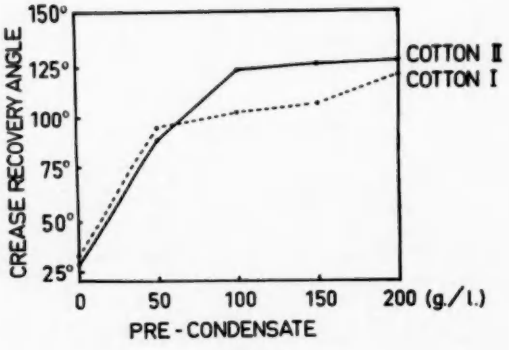


Fig. 3

somewhat different, since the centrifugal force still continues to be present after removal of the liquid.

If we assume that resin deposition in cotton fibers is largely controlled by diffusion processes, it follows that a concentration gradient exists between the precondensate solution which is initially only in the capillaries between the fibers, and the fiber-swelling water, that is, the residual moisture. This system tends to establish an equilibrium. Accordingly, as the water evaporates during drying and the precondensate concentration in the capillaries between fibers increases, the precondensate diffuses into the interior of the fibers. At the same time, water is expelled to the outside. This process is continuous, and because of the communicative system between interfiber capillaries and submicroscopic channels in the fiber, as shown in Figure 1, establishment of equilibrium is possible.

In this manner it is possible to deposit the entire precondensate, or at least a major portion thereof, in the fiber interior during drying. These processes cannot be influenced by pressure. The precondensate is deposited in the fiber interior quite independently of the squeezing effect, provided that the particles are not too large and the concentration of the precondensate is not too high.

The squeezing effect has no direct bearing on the quantity of liquid in the fiber interior, since it affects not only the swelling fluid but the total quantity of the capillary and swelling fluid, that is, the amount of the fluid in the fiber interior and that between the fibers and yarns.

Under standard technical conditions, it is impossible to remove fully the precondensate solution from the capillaries between the fibers by pressure, to say nothing of pressing it into the fiber interior. The deposition is effected quite automatically, so that it can be accomplished by impregnation without any squeezing action.

It is shown that, by impregnation with precondensate solution, crease resistance can be obtained without pressing or squeezing, provided that the rate of precondensate concentration is not unduly high. In this manner the precondensate can be deposited as far as possible in the fiber interior with the result that little or nothing of it remains in the capillaries between fibers.

Obviously, the pressing or squeezing step in the creaseproofing process has definite functions. However, it has no bearing on the production of crease resistance.

For example, the quantity of precondensate applied to a dry fabric can be controlled to a certain extent by squeezing. For economizing on drying costs, it is possible to employ a highly concentrated precondensate and remove the excess solution by squeezing. Also, uniformity of impregnation can be promoted by pressing and squeezing. In the absence of these operations, the period required for impregnation would be increased, particularly when thick and heavy fabrics or materials which are not wetted readily are used. If the precondensate is applied to a wet fabric, the interchange between impregnating solution and water will be accelerated by pressing.

However, first and foremost, it must be emphasized that vertical feed of goods as well as reeling or stocking of unsqueezed materials is practically impossible without the risk of migration of the precondensate. Technically speaking, it follows that such a method would not be practical unless special precautions were taken. For this reason, padding cannot be generally dispensed with in practical creaseproofing finishing.

However, by pressing or squeezing operations the precondensate is carried only as far as the spaces between fibers, that is, to the surface of the fiber, and thence it deposits in the fiber proper by automatic processes referred to above.

To determine whether pressure is, in fact, indispensable, a series of tests was carried out in which mercerized and nonmercerized samples of cotton fabrics were treated with synthetic resin by the conventional padding process with a wet pickup of 80% (Figure 2) and alternatively by the so-called "immersion process" without squeezing (Figure 3); in both cases precondensate solutions of increasing concentrations were employed. The add-on of appropriately diluted precondensate on a fabric sample conducted through immersion rolls and not squeezed but only slightly mangled amounted to approximately 180%. To prevent migration, the fabrics were dried horizontally in these tests. The precondensates employed were a methylol urea compound with a methylol content of 1.3–1.7% and a modified type of urea-formaldehyde resin (methylether). Swelling values [2] are presented in Table I.

It is apparent that immersion without pressure leads to very good crease resistance and antiswelling effect;[3] the hand of a fabric treated in this manner is practically the same as that of a fabric produced

[2] FACHEMFA-method.
[3] DIN-NORM 53890.

TABLE I. Swelling Values, %

	Untreated	Padding 100 g./l.	Padding 200 g./l.	Immersion 200 g./l.
Cotton I	45	31	28	19
Cotton II	52	33	29	20

TABLE II.

	Diameter of rollers, mm. 200	115
Wet pickup, %	64	59
Decreased swelling, %	42	38
Crease recovery angle	110°	101°

by padding. The precondensate penetrated during drying into the interior of the fiber—as described above—in the case of the nonsqueezing process. The assumption that the deposition of the precondensate during drying is controlled by the concentration gradient is verified by the fact that finishing operations carried out under conditions which prohibit the formation of this concentration gradient show little, if any, useful effects. If squeezing is carried out after impregnation with the precondensate, followed immediately (without drying) by curing in an autoclave in the presence of water at 266° F., a normal diffusion of the precondensate into the fiber interior is impossible because the concentration gradient controlling the deposition process is not present. Fabrics subjected to this treatment will lack suppleness, since the resin deposits to a considerable extent on the surfaces of fibers and yarns. In this case the flow of the precondensate is from the inside to the outside.

A further proof of this theory is supplied by the fact that fabrics treated in the normal manner with the precondensate and subsequently dried are cured in a wet steam atmosphere of 212° F. The precondensate, initially deposited in a normal manner, tends to migrate to the exterior and to concentrate on the fiber surface or the outer zones, obviously again due to the flow of the precondensate from the inside to the outside. In such cases, useless fabrics lacking suppleness were obtained.

Relations Between Roll Pressure in Padding and Crease Resistance

The actual functions of pressure in padding operations can be seen by examining the effects obtained by changes in the pressure.

For example, by varying the linear pressure in padding and determining the effects resulting from the various pressures, the values shown in Figure 4 are obtained. These reveal, as anticipated, that the wet pickup drops with an increase in linear pressure; in other words, the quantity of applied resin decreases. In proportion to the quantity of applied resin the effects obtained tend to drop under increased linear pressure with a resultant decrease in wet pickup. It will thus be seen that the results obtained are not governed by the pressure in itself but by the quantity of resin applied, as determined by the pressure employed.

Padding operations under constant linear pressure, but with various squeeze roll diameters, will in the case of large diameters and consequently wider roll passes cause reduced surface pressure and thus also reduced squeezing intensity, resulting in a higher wet pickup. The effects obtained are enhanced in the same ratio, as shown in Table II.

Changing the speed of goods during padding will also result in changing the wet pickup, as shown in Figure 5. Less precondensate is removed when the speed of goods is increased; hence the quantity of resin deposited in the fabric is increased. The crease recovery angle is increased and the swelling values are reduced in the same ratio. Thus it stands to reason that extended duration of pressure will decrease rather than increase the desired effects.

Application of Precondensate by Spraying

Under the circumstances described it could be reasonably expected that it must be possible to impart crease resistance by spraying precondensate on the fabric instead of impregnating or padding it. It would then be possible to apply a precondensate of an appreciable concentration, with resultant savings in drying time and costs. This method would require the homogeneous application of the precondensate, which is a purely technical problem. The materials subjected to spraying treatments should show particularly good absorbent properties.

Cotton fabrics were sprayed with various types of precondensates in increasing quantities by means of a fine spraying nozzle. They were subsequently dried and cured by conventional methods. The results obtained by this treatment are shown in Figures 6 and 7, as well as in Table III.[4] As can be seen from

[4] For obvious reasons, only a small part of the test results could be shown.

the diagrams, the quantity of resin applied or deposited controls the effects obtained.

Absorbent properties of the fabrics employed were such that uniform absorption of 50% of the solution applied by spraying was ensured. Uniform effects were still obtained at a spraying intensity of 40% on the weight of the materials. In view of the results it can be safely said that the crease recovery angle increases when a precondensate of a concentration of up to 300 g./l. is employed, but it tends to drop when this value is exceeded. In all fabrics optimum crease recovery angles were invariably obtained by application of a precondensate of a concentration of approximately 250–300 g./l. At higher concentrations, "one-side effects" were frequently observed; i.e., the crease recovery angles on the sprayed side of the fabric were higher than those on the untreated side.

The apparatus employed is shown in Figure 8. For spraying, Lechler flat fan spraying nozzles [5] made from chrome-nickel steel were used. The tests revealed that a minimum pressure of 3.5–4 atmospheres (equalling 44–57 lb./sq.in.) is necessary to achieve homogeneous distribution of the precondensate solution on the fabrics. In view of this, a spraying tank equipped with a manometer was designed and constructed. Reproducible and acceptable spraying was obtained with this apparatus. Width of fabrics was limited to 35 cm., and the fabric was evenly covered by one spraying nozzle from distances varying between 10 and 15 cm.

[5] Manufactured by Paul Lechler, Stuttgart.

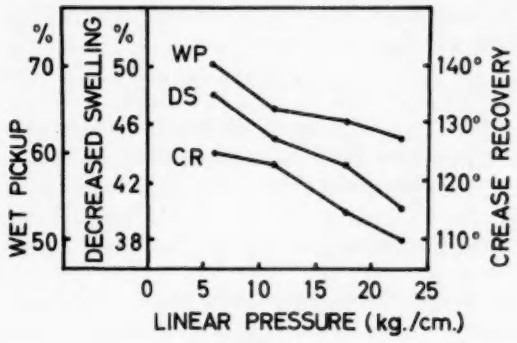


Fig. 4

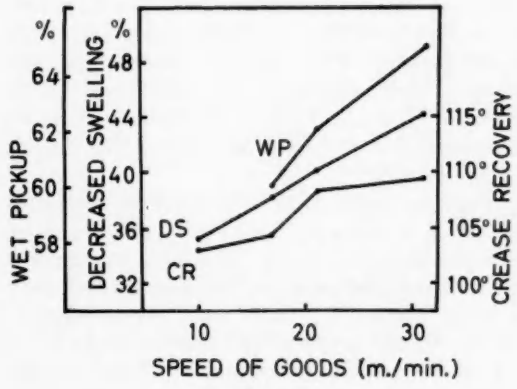


Fig. 5

TABLE III. Swelling Values, %

	Untreated	200 g./l.	300 g./l.
Cotton I	45	24	21
Cotton II	52	25	22

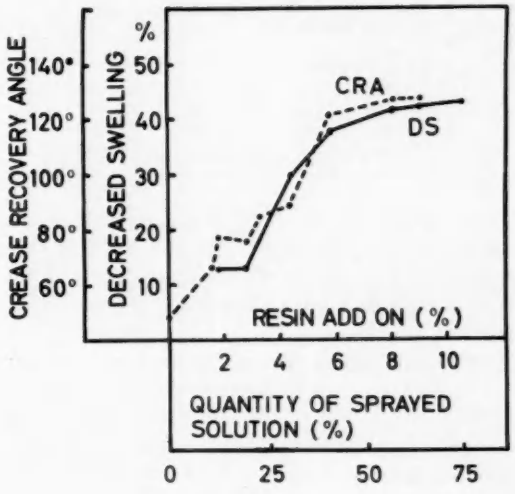


Fig. 6

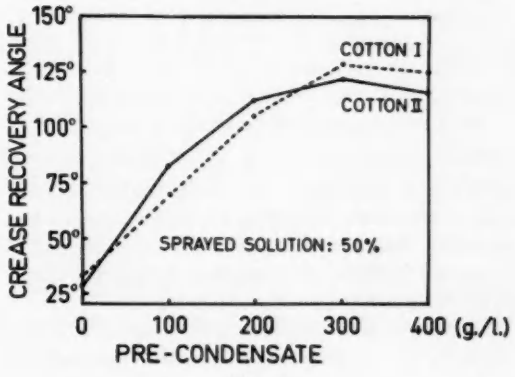


Fig. 7

TABLE IV.

	Crease recovery angle, degrees	
	Cotton I	Cotton II
Untreated	32	28
Padding	108	105
Spraying (50%)	121	118
Immersion	101	102
Resin add-on: 8.5%		

TABLE V.

	Abrasion resistance, rotations	
	Padding	Spraying
Mercerized cotton		
Untreated fabric	422	422
7.5% Resin add-on	326	375
11.5% Resin add-on	276	306
14% Resin add-on	315	452
Cotton (not merc.)		
Untreated fabric	361	361
7.5% Resin add-on	302	312
11.5% Resin add-on	280	305
14% Resin add-on	322	308

The assumption expressed above, that crease resistance can also be obtained by spraying, was thus confirmed. The results also support the idea expressed on the deposition of the precondensate during the drying process.

Generally speaking, the fabric hand was not adversely affected. It was the same in sprayed fabrics as in padded materials. The fabric hand became stiff and hard only if the precondensate solutions employed for spraying were highly concentrated (400 g./l.) and where resin add-on in the fabrics exceeded 12%.

The comparisons in Table IV show that crease resistance is attainable by any one of the three methods.

Comparisons Between Localization and Distribution of Resin in Sprayed and in Padded Fabrics

Fabric samples which have been treated by both methods were examined as to the distribution of resin in yarns and fibers. Spraying was applied with a wet pickup of 55% and padding with a wet pickup of approximately 80%. For the remaining steps, standard finishing methods were employed.

Test results were verified with the aid of Kiton Pure Blue V. The dye was applied simultaneously with the precondensate solution. This presents a method of verification especially developed for the present study. It is assumed that the dye is fixed to the precondensate solution by intermediate electrostatic forces, as shown in Figure 9. The advantage of this method is that hydrolytic migration of the resin cannot take place, as is possible in the case of staining the resin after application.

As is apparent from microscopical investigations of cross sections, no essential differences in resin distribution and deposition can be found between samples treated by either the padding or the spraying method. This is in agreement with the outlined theories. Similar results were obtained from examination of samples treated by the immersion method.

Abrasion Resistance of Finished Fabrics

Abrasion resistance tests were carried out with the Frank-Hauser apparatus. Table V shows the number of abrasive cycles. A comparison of the values obtained for fabrics treated by the padding method with those obtained for sprayed fabrics shows that there is no substantial difference between them. It even seems that the values obtained for sprayed fabrics are slightly superior.

Critical Appraisal of Spraying Method

Assuming that a technically acceptable spraying procedure were available, it would offer the following advantages over padding:

1. No mechanical stresses on fabrics.
2. Reduced driving costs, since less liquor can be applied.
3. Increased processing speed, since the reduced quantity of water would require less time for evaporation in the drying process.

On the other hand, it must be said that by the spraying method it is difficult to achieve the same good results obtained by the padding method when the treated fabrics weigh more than 250–300 g./sq. m. (10.4–12.6 oz./sq. yd.). By the use of humectants or presteaming, the absorbent properties of the fabrics can be enhanced.

In addition, uniform spraying of the precondensate solution on fabrics wider than the spraying range of the nozzle presents certain difficulties. Although a variety of technical solutions have been offered, such as rotary nozzles or nozzles with traverse motion, they do not satisfactorily fulfill present demands.

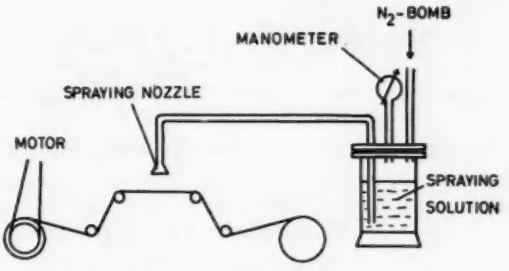
A possible solution to the problem of uniform application would be the use of a spraying or atomizing

chamber, into which the precondensate is introduced. With a suitable layout, this arrangement would permit high production speeds. In addition, a closed spraying chamber offers the advantage of minimizing the offensive effects of formaldehyde. Figure 10 shows a layout of this type.

The fabrics are treated in the presteamer to attain a certain degree of preswelling for easier absorption of the resin applied by spraying. After treatment in the spraying chamber, an air passage has been provided to ensure uniform distribution of the precondensate solution in and on the fabric before drying. The final stages are drying and curing.

It is thought that the spraying method is suitable for finishing goods sensitive to tension and pressure, including ready-made garments.

The spraying process involves two opposing tendencies. On the one hand, a minimum application of liquid is desired, in order to minimize evaporation; on the other, spraying limits the concentration of the precondensate solution. It must be remembered that concentrations exceeding 300–500 g./l., which equals approximately 60% solid contents, are far too viscous and cannot be sprayed through the nozzles. Another difficulty is that the concentrated solutions are not distributed evenly in and on the fabric, giving a "one-side effect" and reduced crease recovery angles. It is therefore recommended that the concentration of the precondensate in practice be held below 300 g./l. This ensures that sufficient quantities of precondensate are applied to fabrics, giving a wet pickup of 45–55%.



SPRAYING DEVICE

Fig. 8

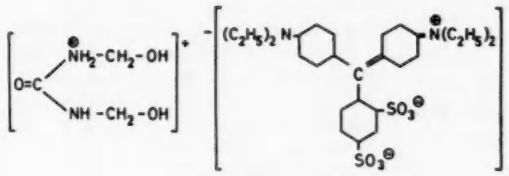


Fig. 9

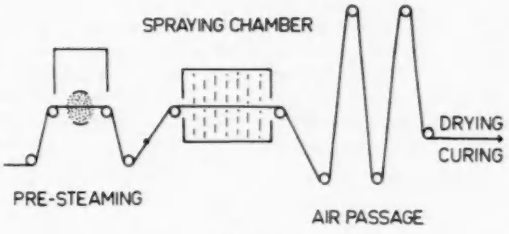


Fig. 10

Summary

The processes leading to resin deposition inside cotton fibers have been discussed, and the theory advanced has been substantiated by a series of tests. It was shown that deposition of synthetic resin in the interior of the fiber is independent of the method of application employed. Accordingly, deposition of the resin and consequently crease resistance and reduced swelling can be achieved by immersion as well as by spraying of the precondensate solution on fabrics, provided suitable equipment is available.

Resin deposition accomplished by the various application methods was made apparent with the aid of an especially developed identification procedure. Since resin deposition was practically uniform in all cases, the fabrics exhibited a fairly equal level of abrasion resistance for all methods of application employed.

While in principle heavy squeezing effects are not absolutely essential for the attainment of crease resistance, this step is obviously required in practice.

New Developments in Epoxide Wash-Wear Finishes for Cotton[1]

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Abstract

A study has been made of a number of epoxides of potential and current utility for the treatment of cotton to produce crease recovery and wash-and-wear properties. The properties imparted to cotton by these products vary greatly with respect to the color of the fabric, the retention of strength for a given level of crease recovery, the rate of hydrolysis of the epoxide in the treating bath, etc. It is in fact unreasonable to consider all epoxides as a class, since they differ as much from one another as they do from the conventional nitrogen-containing finishes. In general, however, they demonstrate resistance to chlorine retention and a high level of durability to all types of laundering, including that used by commercial laundries.

One of the most promising epoxides examined was vinylcyclohexene dioxide, which imparted a desirable combination of properties to cotton when used alone or in 2:1 blends with most commercially used nitrogenous resins.

Some treatments of cotton were performed with 1,1,3-tris-(2,3-epoxypropoxy)-butane. This tri-epoxide contains an acid-labile acetal linkage, which can be readily hydrolyzed. The properties of cotton treated with this epoxide were examined before and after hydrolysis, and provided confirmatory evidence for the important role of cross-linking in improving the properties of cellulose with resin treatments.

Introduction

The explosive growth of the use of wash-and-wear finishes for the cellulosic fibers has created a sizable market for chemicals, and has stimulated intense activity in the development of new finishes, especially for cotton. In the main, this work has been directed towards the improvement of the properties imparted by the finishes which have been used for some time in this field; it is generally agreed that the deficiencies of the treated fabrics include susceptibility to chlorine retention, inadequate durability to commercial laundering, and a relatively high loss of strength or other necessary physical properties after treatment. Secondary problems that exist to one degree or another in some commercial finishes include tendency toward formation of odors, yellowing after treatment or in use, and a tendency to pick up soil rapidly.

It was recently shown by Schroeder and Condo [8] that epoxy resins could be successfully used to enhance the crease recovery and wash-and-wear properties of cotton fabrics. It was demonstrated by these workers that cotton treated with epoxy resins was not susceptible to chlorine retention and that the finish was remarkably durable to laundering or other treatments to which the fabric might reasonably be subjected. The product proposed for this use was, however, relatively high in cost and required relatively high add-ons for adequate treatments. The possibility of using blends of epoxides and the commonly used nitrogenous resins was explored by Gagliardi and Shippee [5], who showed that such blends reduced the cost of a commercial treatment and provided good resistance to chlorine retention. They left unanswered, however, the question of durability to commercial laundering. Admittedly, this should be a relatively minor problem in a garment designed to be laundered and dried at home, but consumer experience suggests that such garments are in fact sometimes sent to commercial laundries.

[1] Presented at the Chemical Finishing Conference of the National Cotton Council of America, Washington, D. C., October 7, 1959.

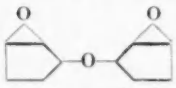
The present paper is intended to extend some of the observations of Schroeder and Condo and Gagliardi and Shippee and to comment on the properties of a number of very different epoxides, including some of those mentioned by these earlier authors. It also presents some evidence concerning the mechanism of reaction of epoxides with cellulose and describes some practical results obtained with different epoxides and their blends with the conventional nitrogenous finishes.

Materials and Methods

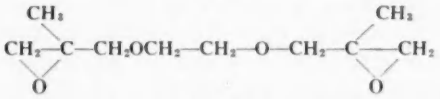
Materials

The structures and designations of the epoxides discussed below are presented in Table I. As a matter of convenience, they will sometimes be referred to below by the designations given in parentheses after their chemical names. The "commercial epoxy resin," a diglycidyl ether, was purchased on the open market. The other four products were prepared in the Research Department of the Union Carbide Chemicals Company. One of these, vinylcyclohexene dioxide, will shortly be made available commercially as UCET Textile Finish 11–74.[2]

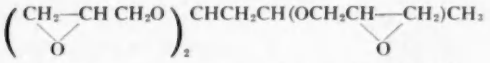
TABLE I. Structures and Designations of Some Epoxides Discussed in This Paper



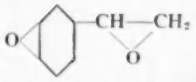
Bis-(2,3-epoxycyclopentyl) ether (Epoxide I)



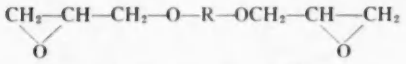
1,2-Bis-(2,3,-epoxy-2-methylpropoxy) ethane (Epoxide II)



1,1,3-Tris-(2,3-epoxypropoxy)-butane (Epoxide III)



Vinylcyclohexene dioxide
(Epoxide IV; UCET Textile Finish 11–74)



(commercial epoxy resin)

The solubilities of the five epoxides are presented in Table II. Epoxide I is virtually insoluble in water. The commercial epoxy resin contains a minor fraction which is insoluble in water and necessitates the preparation of an emulsion system for treating textiles [9]. The three remaining products have a relatively high water solubility, hence are suitable for preparing textile treating baths directly.

The cotton fabrics used in this work were an 80 × 80 cotton print cloth and a 157 × 59 cotton broadcloth. Both had been mercerized and bleached and were in a prepared state suitable for resin treatment. The physical properties of the untreated fabrics are presented at the appropriate place in the tables given below.

Methods

For the three soluble epoxides, preparation of a treating bath simply involved dissolving the product in water, followed by addition of an appropriate catalyst. The commercial epoxy resin was emulsified with the help of 0.65% of polyvinyl alcohol according to the directions supplied by the manufacturer. Epoxide I is water-insoluble, but it can be made into a treating bath by appropriate emulsification. In addition, when a non-ionic emulsifier such as Tergitol Non-Ionic XD [2] was added to the system in an amount greater than 50% of the weight of the epoxide, a micellar solution of Epoxide I was obtained which showed a typical schlieren effect. Such

[2] Union Carbide Corporation trademark.

TABLE II. Solubility of Epoxides in Water

Epoxide	Solubility	Treating bath
I	0.3%	Emulsion or micellar solution
II	Completely miscible	Aqueous solution
III	Completely miscible	Aqueous solution
IV	18%	Aqueous solution
Commercial epoxy resin	Contains minor insoluble portion	Emulsion (polyvinyl alcohol emulsifier)

micellar solutions are free of the instability problems common to many emulsions. Accordingly, micellar solutions were used for all of the treatments involving this epoxide.

Conventional procedures were used for padding (double dip, double nip), tentering on small frames, drying, and curing. Conditions for the latter two operations varied from product to product, and are given in the appropriate tables.

Breaking strength measurements on the treated, laundered samples were made by the raveled strip method [1], using the Instron tester. Tearing strength measurements were performed on the Elmendorf machine. Crease recovery was measured with the Monsanto instrument [2]. These and other physical tests were made on samples which had been scoured after treatment by washing in a home washing machine at the "hot" setting, with a built anionic commercial detergent. The samples were then tumble dried at the "hot" setting and conditioned at 65% relative humidity and 70° F. before test.

Measurements of yellowness index were performed on the Hunter Reflectometer, the yellowness index being defined by the relationship

$$\text{Yellowness Index} = \frac{A - B}{G}$$

Where A, B, and G represent the reflectances of the sample with amber, blue, and green filters.

Wash-and-wear ratings were performed by evaluating subjectively photographs of the test specimens. The latter were illuminated with the DuPont lighting arrangement [4], but with the light 11 in. from the wall; photographs were made with a Polaroid Land Camera 16 in. from the specimen. The photographs of the test specimens were in turn rated against photographs of the same size taken of the Eastman Chemical Company standards. The results represent the averages of the ratings assigned by at least three observers. The scale ranges from 1 (very mussy, untreated control) to 5 (smooth, as ironed). Wash-and-wear ratings are given only to the nearest unit, since the precision of measurement does not justify the use of two significant figures.

Results and Discussion

Susceptibility of Epoxides to Hydrolysis

Epoxides vary enormously in their rates of reaction with themselves or with cellulose, as well as in their rates of hydrolysis in aqueous systems. The rate of hydrolysis of an epoxide such as limonene dioxide is so rapid in slightly acidic solutions that

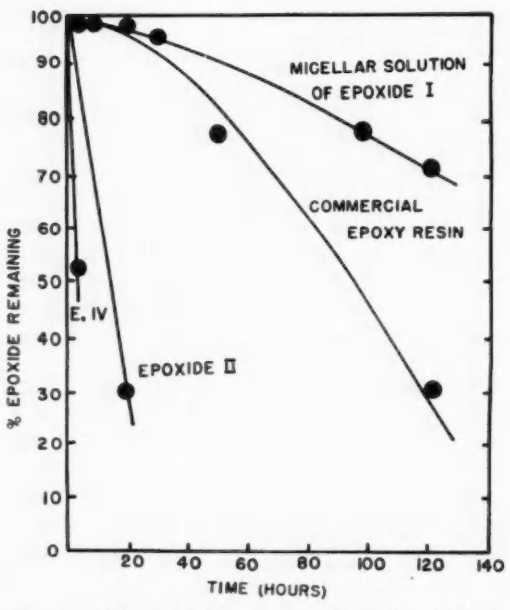


Fig. 1. Hydrolysis of epoxide treating baths at 25° C. Systems contained 1.6% zinc fluoborate.

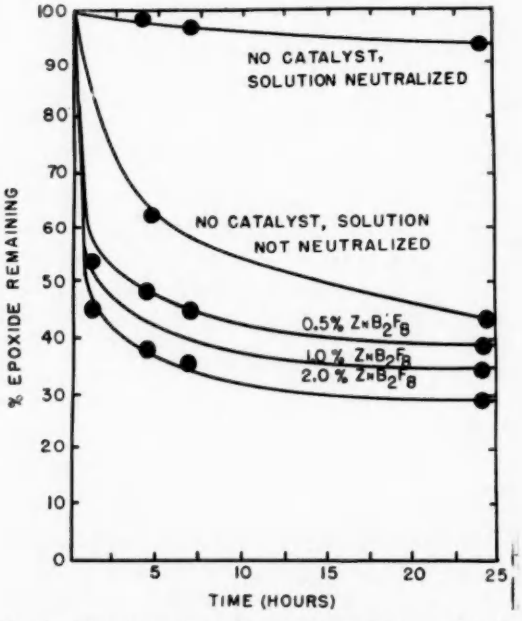


Fig. 2. Hydrolysis of solutions of vinylcyclohexene dioxide in the presence and absence of zinc fluoborate catalyst.

a typical treating bath may actually become hot before it is used. Figure 1 compares the rate at which epoxy groups hydrolyze for several of the compounds discussed in this paper, in typical treating baths at 25° C. In these experiments, the concentration of the epoxide (or epoxy resin) was 20% for Epoxide I and 15% for the other epoxides listed. The system contained 1.6% of zinc fluoborate catalyst; the pH was approximately 3.5. The loss of epoxide groups was determined by titration with hydrogen bromide in anhydrous acetic acid.

As shown by the data in Figure 1, Epoxide I was extremely resistant to hydrolysis, approximately 70% of the epoxy groups remaining after about 5 days of aging. The commercial epoxy resin was less stable, but still sufficiently resistant to hydrolysis for practical purposes. The two remaining products tested, particularly Epoxide IV (vinylcyclohexene dioxide), lost epoxy groups very rapidly. Additional results for the latter compound are presented in more detail in Figure 2. The sample studied contained a small amount of acid, and as shown by the second curve from the top, an aqueous solution of this epoxide hydrolyzed at a rapid rate even in the absence of catalyst. The presence of increasing amounts of zinc fluoborate catalyst further increased the rate of loss of epoxy groups. In the absence of catalyst, however, the neutralized solution remained quite stable, as shown by the uppermost curve.

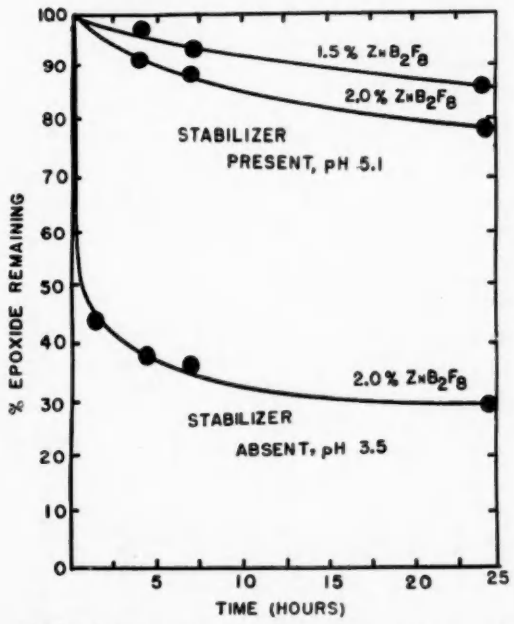


Fig. 3. Effect of UCET Stabilizer TF on the rate of hydrolysis of vinylcyclohexene dioxide treating baths.

It is easily demonstrated that the rate of hydrolysis of Epoxide IV (vinylcyclohexene dioxide) and other epoxides can be controlled by adjusting the pH of the treating bath. Several buffer systems were studied. To insure compatibility with the catalyst, UCET Stabilizer TF[2] was developed. Figure 3 contrasts the rapid rate of breakdown of Epoxide IV in the presence of catalyst and the absence of buffer with the satisfactory level of stability which can be obtained by the addition of stabilizer to bring the pH to 5.1. The use of such stabilizers facilitates the practical use of some epoxides which react readily with cellulose and which otherwise possess a desirable combination of properties.

It is interesting to note that similar considerations apply even when this epoxide is used in a blend with a resin such as dimethylolethylene urea; the need for and successful use of a stabilizing agent for such a blend are shown in Figure 4.

As might be expected, the loss of epoxide groups with increasing age of a treating bath containing Epoxide IV is reflected in the properties of the treated fabrics. Table III shows that, after 4 hr. of standing, a treating bath which gave a high level of crease recovery and wash-and-wear properties lost most of its effectiveness; the measurements of breaking strength indicate that the product is no longer cross-linking to the same extent. In contrast, a stabilized bath produced an entirely satisfactory treatment after the same 4-hr. period of aging.

Effect of Treating Conditions on Properties of Cotton Treated with Epoxide IV

Table IV shows the effect of a broad range of curing conditions on the treatment of cotton with Epoxide IV. These results reveal the rather surprising fact that a substantial level of treatment can be attained at curing temperatures as low as 100° C. when the curing time is extended and the catalyst concentration is high. Curing can be effected at still lower temperatures, such as 75° C.,[3] but impracti-

[3] It is rather surprising that an effective cure can be obtained at temperatures as low as this. It has been suggested [9] that the active catalyst in zinc fluoborate in boron trifluoride, produced by thermal breakdown of the zinc fluoborate. Since the decomposition temperature of zinc fluoborate is given as approximately 150° C. [9], the present results suggest that the zinc fluoborate itself is the active catalyst.

cally long times of cure and high catalyst concentrations are required. The data indicate that satisfactory curing can be obtained over a surprisingly broad range of conditions and that, by the use of a sufficient quantity of catalyst, the problems introduced by the high volatility of this epoxide can be minimized. Practical considerations and the properties of the treated fabric suggest that a good balance can be obtained by curing at 140° C. for 3 min. in the presence of 0.5% (dry) zinc fluoborate catalyst on the weight of fabric. Under these conditions, measurements of the dry weight of the treated fabric indicate that approximately 60–75% of the epoxide remains on the fabric. It would, of course, be highly desirable to increase this figure, but yields of this order of magnitude are not uncommon for commercially used nitrogenous resin treatments.

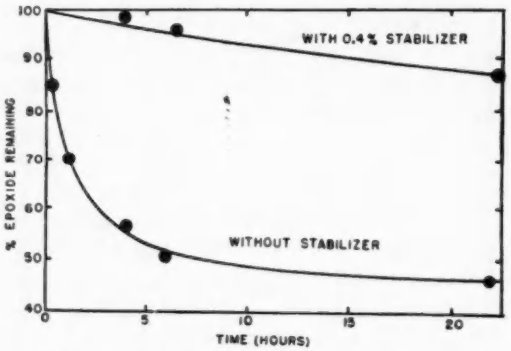


Fig. 4. Effect of UCET Stabilizer TF on the rate of hydrolysis of a blend of vinylcyclohexene dioxide and dimethylolethylene urea (2:1) in the presence of 1% zinc fluoborate.

Properties of Cotton Treated with Various Epoxides

Table V compares the properties of cotton print cloth treated with four epoxides and a commercial epoxy resin under conditions which left approximately the same dry solids on the fabric. The conditions used in applying the commercial epoxy resin were those suggested by the manufacturer, whereas for each of the four other products the optimum

TABLE III. Effect of Age of Treating Bath on the Properties of Cotton Treated with Epoxide IV

Solution concentrations and wet pick-up were adjusted to give nominal dry add-on of 15% Epoxide IV, 2.0% zinc fluoborate, and UCET Stabilizer TF in amounts as indicated below. Samples were dried at 77° C. for 2.5 min. and cured at 140° C. for 3 min.

Stabilizer, %	Age of bath, hr.	Actual add-on, %	Wash-wear index	Crease recovery, %	Breaking strength retained, %
0	0	8.1	4	69	51
0	4	5.7	2	51	80
0.2	4	8.2	5	69	57
Untreated cotton	—	—	2	43	100 (45 lb.)

TABLE IV. Effect of Curing Conditions on the Properties of Cotton Print Cloth Treated with Epoxide IV

Samples were cured for 3 min., except as noted.

Curing temperature, ° C.	ZnB_2F_8, %	Actual add-on, %	Wash-wear index	Crease recovery, %	Breaking strength retained, %
100	2	5	3	58	72
100*	2	8	4	63	66
140	0.5	8	4	66	60
140	2	8	5	69	58
140	3	6	4	65	62
200	0.5	9	4	67	43
200	3	15	4	66	45

* Cured for 60 min.

conditions were chosen from a series of experiments similar to those described in Table IV. The differences in the functional properties produced by these five products were relatively small, the most conspicuous being the high yellowness index of the fabric treated with Epoxide I. In addition, both Epoxides III and IV imparted a slightly more favorable balance between crease recovery and retention of breaking strength than the other products examined.

The conspicuous yellowing of the fabric treated with Epoxide I suggested that there may be important differences among epoxides in their tendency toward yellowing the fabric; accordingly a series of experiments was performed to investigate this factor in some detail. In these measurements, treated fab-

TABLE V. Properties of Cotton Print Cloth Treated with Various Epoxides under Optimal Conditions

Solution concentrations and wet pick-up were adjusted to give nominal dry add-on of epoxide solids and catalyst as indicated below. The samples were dried at 75° C. for 3 min. and cured at temperatures indicated for 3 min.

Epoxide	Nominal add-on, %		Curing temperature, ° C.	Actual add-on, %	Wash-wear index	Yellowness index	Crease recovery, %	Breaking strength retained, %
	Epoxide	ZnB_2F_8						
I	10	2.0	140	8.6	4	0.10	71	54
II	15	1.0	120	8.3	4	.04	71	60
III	15	1.0	120	10.4	4	.04	83	59
IV	13	0.6	140	7.7	4	.03	71	63
Commercial epoxy resin	13	0.6	160	9.6	4	.04	75	52
Untreated cotton print cloth	—	—	—	—	1	.04	43	100 (54 lb.)

TABLE VI. Effect of Dry Heat on the Yellowness of Variously Treated Print Cloth *

Samples were heated at temperatures indicated for 5 mins.

	Yellowness index		
	350° F.	400° F.	450° F.
Dimethylolethylene urea (zinc nitrate catalyst)	0.13	0.28	0.45
Dimethylolethylene urea (amine hydrochloride catalyst)	.12	.26	.45
Triazone	.19	.56	dark brown
Triazine	.15	.25	.47
Epoxide IV	.11	.22	.33
Epoxide I	.23	.40	.51
Commercial epoxy resin	.15	.34	dark brown
2:1 Blend of Epoxide IV and			
Dimethylol ethylene urea	.13	.26	.38
Triazone	.23	.57	.66
Triazine	.15	.31	.43
Modified melamine formaldehyde	.13	.43	.58
Dimethylol hexahydropyrimidone-2	.13	.24	.38
Untreated cotton print cloth	.12	.28	.41

* The conditions of treatment of these samples are given in Table V (Epoxide I, Epoxide IV, and commercial epoxy resin), Table X (dimethylolethylene urea, triazone, and triazine), and Table XI (blends).

rics were heated between the platens of a Carver press for 5 min. at temperatures of 350°, 400°, and 450° F. The yellowness index of the scorched fabrics was then measured with the Hunter Reflectometer, as described above. As a matter of general interest, the experiments were extended to include not only a comparison of three of the epoxy-containing products, but a number of commercial nitrogenous resins and blends of Epoxide IV with these products. The results of these experiments are shown in Table VI. The data indicate that Epoxide I did indeed impart an extreme tendency toward yellowing to the treated fabric, and this tendency was also present in the fabric treated with the commercial epoxy resin. The dimethylolethylene urea produced no such result, the treated fabric yellowing at the same rate as the untreated control. Surprisingly, the fabric treated with Epoxide IV yellowed at a lower rate than the untreated control, indicating that the treatment protected the cellulose against scorching. Among the remaining treatments, the triazone yellowed severely, alone or in the blend, and the blend containing the

TABLE VII. Reaction of Epoxide I with Ethylene Glycol and Isopropanol

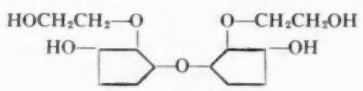
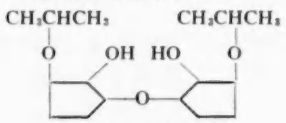
Ethylene Glycol + Epoxide I	Isopropanol + Epoxide I
Reaction conditions:	Reaction conditions:
1. Charge (molar ratio) Epoxide I —1 Ethylene glycol—5 Water —4	1. Charge (molar ratio) Epoxide I —1 Isopropanol—10
2. Zinc fluoborate—1%	2. Zinc fluoborate—1%
3. 100° C.—2 hr.	3. 80° C.—1 hr.
Exp. results:	Exp. results:
Molecular weight 320	Molecular weight 340 Hydroxyl equivalent weight 171
Possible Structure:	Possible structure:
	
Molecular weight 306	Molecular weight 302 Hydroxyl equivalent weight 151

TABLE VIII. Effect of Hydrolysis on the Properties of Cotton Treated with Epoxide III

Solution concentration and wet pick-up adjusted to give nominal dry add-on of 10.8% Epoxide III and 1.2% zinc fluoborate. Samples were dried at 75° C. for 3 min. and cured at 140° C. for 3 min.

Treatment	Crease recovery, %	Yarn resilience† after 3% extension: Length recovery, %	Yarn resilience† after 3% extension: Work recovery, %	Solubility in cupriethylene diamine, %
None (control)	43	44	38	100
Epoxide III	72	59	50	~0
Epoxide III plus acid hydrolysis*	35	49	42	65
Control after acid hydrolysis*	42	45	36	100

* Hydrolyzed in 0.1 *N* HCl for 30 min. at 80° C.

† Sample extended to 3% (at 20%/min.) on the Instron machine and immediately retracted to zero load. Measurements made at 65% relative humidity.

modified melamine formaldehyde also showed this tendency to a lesser degree.

The significance of the results outlined in Table VI should perhaps not be overemphasized, since the conditions of test are rather drastic. However, temperatures in the neighborhood of 450° F. are commonly encountered in an iron at the "cotton" setting as well as in a press. Accordingly, the data may be

TABLE IX. Effect of Add-On on the Properties of Print Cloth Treated with Epoxide IV, a Commercial Epoxy Resin, or 2:1 Blends of Epoxide IV with Dimethylolethylene Urea or a Triazone

Nominal resin add-on, %	Actual add-on, %	Yellowness index	Wash-wear index	Crease recovery, %	Breaking strength retained, %
Epoxide IV, (vinylcyclohexene dioxide)					
13	7.6	0.04	4	68	62
8	4.0	.03	3	61	60
4	2.5	.04	2	55	62
Commercial epoxy resin					
13	9.2	.05	4	73	49
8	4.4	.04	3	59	51
4	2.1	.05	3	54	53
Epoxide IV + dimethylolethylene urea (2:1)					
8.5	5.8	.04	5	72	52
5.9	4.6	.04	4	66	58
4.2	3.5	.05	3	64	52
2.1	3.2	.04	3	58	50
1.1	1.8	.04	2	54	54
Epoxide IV + triazone (2:1)					
10.0	6.0	.04	5	69	67
8.5	3.9	.04	5	69	60
7.5	4.1	.04	4	59	62
6.0	3.9	.04	4	60	65
5.0	3.1	.05	3	58	65
Control		.04	1	43	100

TABLE X. Initial Properties of Cotton Print Cloth Treated with Epoxide IV and Various Commercial Finishes; Commercial Level of Treatment

All samples were dried at 75° C. for 3 min. and cured at temperatures indicated for 3 min.

Treatment (nominal add-on)	Curing temperature, ° C.	Actual add-on, %	Yellowness index	Wash-wear index	Crease recovery, %	Breaking strength retained, %
5.5% Dimethylolethylene urea, 0.5% zinc nitrate	160	4.8	0.02	4	76	52
5.5% Dimethylolethylene urea, 0.5% amine hydrochloride	160	4.3	.04	4	74	56
7.2% Triazone, 2.0% catalyst	150	5.8	.03	4	75	62
5.5% Triazine, 2.2% catalyst	180	4.2	.03	4	72	50
13% Epoxide IV, 0.6% zinc fluoborate, 0.3% stabilizer	140	7.7	.03	4	71	63
13% Commercial epoxy resin, 0.6% zinc fluoborate, 0.7% polyvinyl alcohol	160	9.6	.04	4	75	52
Untreated cotton print cloth	—	—	.04	1	43	100 (52 lb.)

TABLE XI. Initial Properties of Cotton Print Cloth Treated with 2:1 Blends of Epoxide IV and Commercial Finishes; Commercial Level of Treatment

Solution concentrations and wet pick-up were adjusted to give nominal dry add-on of 7.5% resin solids of a 2:1 blend of Epoxide IV and the commercial resins indicated below, 0.3% stabilizer, and zinc fluoborate as indicated below. The samples were dried at 75° C. for 3 min. and cured at temperatures indicated below for 3 min.

Blend	ZnB_2F_8 %	Curing temperature, ° C.	Actual add-on, %	Yellowness index	Wash-wear index	Crease recovery, %	Breaking strength retained, %
Epoxide IV plus							
Dimethylolethylene urea	0.5	140	4.4	0.03	5	73	61
Triazone	1.5	140	4.7	.05	4	72	57
Triazine	1.5	140	5.1	.04	4	72	57
Modified melamine formaldehyde	1.0	120	4.1	.04	4	69	61
1,3-Dimethylol hexahydropyrimidone-2	1.0	140	4.3	.04	4	71	58
Untreated cotton print cloth	—	—	—	.04	1	43	100 (53 lb.)

taken as providing some indication of the tendency of treated fabrics to darken after prolonged or severe ironing.

Some Comments on the Mechanism of Reaction between Epoxides and Cellulose

The mechanism of the reaction by which resin treatments impart crease recovery and wash-and-wear properties to cellulosic fabrics has never been established with certainty, but it seems reasonable from the evidence to assume that it must involve cross-linking. While some compounds containing a single methylol group have imparted improved properties to cotton or rayon [11], such experiments are suspect in view of the fact that free formaldehyde, a cross-linking agent itself, can be easily detected in the curing operation. It is quite significant, however, that successful resin treatments make the cellulose partly or completely insoluble in solvents for cellulose and that heavy treatments with monoepoxides do not produce a fabric with a reasonable level of crease recovery or wash-and-wear properties [6].

The experiments on model compounds outlined in Table VII contain some evidence which is strongly suggestive of cross-linking. In these experiments, ethylene glycol or isopropanol was reacted with Epoxide I, with a high molar ratio of the hydroxyl-containing compound to the epoxide. In both experiments, one containing a considerable quantity of water and the other essentially anhydrous, the molecular weight of the product obtained suggests that the principal reaction is one in which one molecule of diepoxide reacts with two molecules of the glycol or alcohol. The equivalent reaction in cellulose would be the formation of a cross link between two hydroxyl groups on cellulose chains.

Some experiments conducted with Epoxide III are also of interest in this connection. This tri-epoxide contains an acetal linkage which can be hydrolyzed with acid. Thus, while the ether linkages formed between the epoxide and the cellulose are quite stable to hydrolysis, it should be possible to treat the fabric and then to break cross links at the acetal linkage by a suitable hydrolytic procedure; treatment with 0.1 *N* hydrochloric acid for 30 min. at 80° C., conditions similar to those used for "stripping" commercial resin treatments, was chosen for this purpose.

The results of these experiments are outlined in Table VIII. It can be seen from these data that the treatment with Epoxide III produced a high level of crease recovery, increased the resilience of the yarns at a low extension, and made the treated cotton substantially insoluble in cupriethylene diamine, which is a solvent for cellulose. Hydrolysis with acid reduced the crease recovery to that of the control, reduced the resilience of the yarns, and made the sample soluble in cupriethylene diamine to the extent of about 65%. These results are strongly suggestive of cross-linking by the tri-epoxide and indicate that the improvement in properties is indeed a result of cross-linking.

Practical Treatments with Epoxides and Blends

Effect of Add-On

Table IX shows the effect of add-on on the initial properties of cotton print cloth treated with two epoxide-containing compounds and two blends of Epoxide IV with commercial nitrogenous resins. As shown by these data, both of the epoxides require a nominal add-on of 10–12% to produce a commercially acceptable result, in agreement with the data of previous workers [8]. In accord with the work of Gagliardi and Shippee [5], the use of a blend containing two parts of epoxide to one part of a triazone or dimethylolethylene urea produced a marked increase in the efficiency of the treatment, so that a nominal add-on of the order of magnitude of 6–8% was required to obtain a commercial level of treatment. These results should be compared directly with those presented in Table X, which lists commercial level treatments with a number of widely used resins and two epoxides, and with Table XI, which summarizes the results obtained with blends of Epoxide IV and five commercial resins. In the treatments involving the commercial products, the recommendations of the manufacturer were followed, but where a blend was used, the catalyst was zinc fluoborate and the curing conditions were based on preliminary screening experiments.

It can be seen by comparing Tables IX, X, and XI that the use of a blend of Epoxide IV resulted in a commercial level of treatment with total resin solids slightly greater than that required for the nitrogenous resins. However, since the principal component of the blends was the epoxide, these combinations still suffer from a significant price disadvantage. It is important, therefore, to examine the chlorine retention properties, durability to commercial laundering, and other properties to see whether this increased cost would be justified.

TABLE XII. Chlorine Retention of Cotton Print Cloth Treated with Epoxide IV, Alone or in Blends, and Various Commercial Resins

Samples were subjected to Smith's accelerated aging test* followed by AATCC Test 69-1958.

Treatment	Initial breaking strength retained, %	Breaking strength retained after chlorine retention test, %	
		Based on untreated strength	Based on treated strength
Dimethylolethylene urea (zinc nitrate catalyst)	52	24	46
Dimethylol ethylene urea (amine hydrochloride catalyst)	56	12	21
Triazone	62	52	84
Triazine	50	46	92
Epoxide IV (vinylcyclohexene dioxide)	63	63	100
Commercial epoxy resin	52	53	102
2:1 Blend of Epoxide IV and Dimethylol ethylene urea	61	61	100
Triazone	57	56	98
Triazine	57	50	88
Melamine formaldehyde	64	61†	95
Modified melamine formaldehyde	61	59	97
Dimethylol hexahydropyrimidone-2	58	52	90
Untreated cotton print cloth	100	93	—

* 80° C., 16 hr., approximately 100% RH.
† Chlorine test turned sample yellow.

Chlorine Retention

The chlorine retention properties of print cloth treated with a number of commercial resins, two epoxides, and several blends of Epoxide IV and commercial nitrogenous resins are summarized in Table XII. The test used involved the accelerated aging at high relative humidity and 80° C. suggested by Smith [10], followed by the standard AATCC Test 69–1958. It can be seen that this combination produced rather severe chlorine retention and loss of strength in the fabric treated with dimethylolethylene urea, even with the "hard cure" produced with a zinc nitrate catalyst. Neither epoxide, nor any of the blends of Epoxide IV and the commercial resins,

TABLE XIII. Durability to Acid Stripping of Cotton Print Cloth Treated with Epoxide IV, Alone or in Blends, and Various Commercial Resins

Treatment	Initial crease recovery, %	Crease recovery after: Urea-H_3PO_4* "stripping," %	Crease recovery after: HCl† "stripping," %
Dimethylolethylene urea	78	47	44
Triazone	74	46	44
Triazine	74	52	48
Modified melamine formaldehyde	72	53	53
Dimethylol hexahydropyrimidone-2	76	48	47
Epoxide IV (vinylcyclohexene dioxide)	66	69	68
Commercial epoxy resin	72	69	67
2:1 Blend of Epoxide IV and			
Dimethylolethylene urea	70	50	49
Triazone	70	60	57
Triazine	69	62	56
Modified melamine formaldehyde	67	61	58
Dimethylol hexahydropyrimidone-2	72	60	56
Untreated cotton print cloth	43	—	—

* 1.3% H_3PO_4, 5% urea, 77° C., 5 min.
† 0.1 *N* HCl, 80° C., 25 min.

TABLE XIV. Initial Properties of Commercial Wash-and-Wear Shirts and Shirts Treated with Epoxide IV (UCET Textile Finish 11–74)

Shirt	Wash-wear index	Yellowness index	Crease recovery: Warp, %	Crease recovery: Filling, %	Breaking strength: Warp, lb.	Breaking strength: Filling, lb.	Tearing strength, filling, g.
Epoxide IV*	4	0.04	68	68	53	29	760
Commercial Shirt A	4	−.02	68	67	57	30	770
Commercial Shirt B	3	−.01	65	66	51	29	606
Commercial Shirt C	4	−.02	69	75	56	34	820
Commercial Shirt D	4	−.02	82	71	47	24	490

* Treated with 11.1% Epoxide IV, 0.5% zinc fluoborate, 1.0% Moropol 700 (solids), and 0.6% Tergitol Non-Ionic NPX. Fabric was dried at 75° C. for 3 min. and cured at 140° C. for 3 min.

showed chlorine retention under these rather severe conditions. The triazone showed a lower level of chlorine retention, while the triazine, which had a rather high loss of strength after treatment, was quite resistant to the conditions of the chlorine retention test. The relative chlorine resistance of these two types of finish has been the subject of some controversy in the literature [3, 12].

Durability to Acid Hydrolysis

Wash-and-wear finishes require resistance to acid hydrolysis in order to sustain repeated or even occasional commercial laundering. This requirement arises from the use by commercial laundries of an acidic souring operation, the pH of which can be shown to vary widely between typical commercial establishments [7]. In order to test this important property, in which most of the commercial nitrogenous finishes are known to be deficient, the following two laboratory procedures were used.

1. Immersion for 25 min. in 0.1 *N* HCl at 80° C.
2. Immersion for 5 min. in a solution containing 1.3% of phosphoric acid and 5% of urea at 77° C.

The first of these is often used in laboratory work to determine the add-on of commercial nitrogenous resins. The second is frequently used by mills to strip cotton fabric which has been overtreated or unevenly treated, so as to permit retreatment; it has been used for the present purpose by Cooke and Roth [3]. Both procedures are admittedly severe, and can be considered to represent the equivalent of numerous souring operations in commercial laundering. Thus, resistance to these tests should represent a higher level of durability to acid souring than would be required in repeated commercial laundering.

Table XIII shows the effect of the two acid stripping procedures on the crease recovery of cotton treated with blends of Epoxide IV and several commercial nitrogenous resins, as well as with the nitrogenous resins and two epoxides alone. Examination of these results reveals the following points of interest.

1. There was good general agreement between the results of the two tests, although the HCl stripping test was slightly more severe.

2. The crease recovery of fabrics treated with the commercial nitrogenous resins was reduced almost to

TABLE XV. Wash-and-Wear Properties of Shirts After Laundering and Service

Treatment	Wash-wear index (tumble dried)*						Wash-wear index (drip dried)†				
	Original	10 Cycles	20 Cycles	30 Cycles	40 Cycles	50 Cycles	10 Cycles	20 Cycles	30 Cycles	40 Cycles	50 Cycles
Laundered commercially											
Epoxide IV	4	4	3	3	3	(41)‡	4	4	3	3	—
Epoxide IV	4	3	3	3	3	(44)	4	4	3	4	—
Commerical Shirt A	4	2	2	1	1	(40)	3	3	2	2	—
Commerical Shirt C	4	2	1	(20)	—	—	4	3	—	—	—
Commerical Shirt D	4	2	2	**	—	—	3	2	—	—	—
Home washed and tumble dried											
Epoxide IV	4	4	3	3	3	4	4	4	3	4	4
Epoxide IV	4	4	3	3	4	4	4	4	4	4	4
Commercial Shirt A	4	4	3	2	3	3	4	3	3	4	4
Commercial Shirt D	4	4	3	3	2	—	4	4	—	—	—
Home washed and line dried											
Epoxide IV	4	3	3	3	3	3	4	4	3	4	3
Epoxide IV	4	4	3	3	3	3	4	4	3	3	4
Commercial Shirt B	3	—	—	—	—	2	—	—	—	—	3

* Washed in automatic washer using extraction cycle; dried in tumble dryer.
† Washed in automatic washer using no extraction cycle; drip dried on hanger.
‡ Number in parentheses refers to number of laundering cycles after which shirt became unwearable.
** Evaluation stopped after 20 laundering cycles.

that of the control for three of the nitrogenous resins, and was reduced less, but very substantially, for the modified melamine formaldehyde and the triazine.

3. The fabrics treated with Epoxide IV or the commercial epoxy resin retained almost all of their crease recovery.

4. Among the blends, the addition of Epoxide IV to the commercial nitrogenous resins produced some improvement in each case, the least improvement being shown by the blend with dimethylolethylene urea.

These results suggest that the stripping procedures are valid for predicting the results of repeated commercial souring in laundering. They indicate that blends of Epoxide IV with commercial resins (such as the triazine, triazone, or modified melamine formaldehyde) should perform more adequately with respect to hydrolysis in commercial laundering than do the commercial nitrogenous resins alone.

Experiments on Men's Shirts

In order to obtain information on the performance of treated cotton in actual use, a small-scale service test was run on men's wash-and-wear shirts. Results are currently available only for shirts treated with Epoxide IV in comparison with a number of commercial shirts now on the market, but these experiments are currently being extended to include additional experimental finishes, particularly those containing blends of this epoxide and commercial nitrogenous resins.

The initial properties of the shirts examined in this work are presented in Table XIV. The treatment with Epoxide IV included a polyethylene softener, but no fluorescent brightening agent or bluing. Accordingly, it had a small positive yellowness index (0.04), identical with that of the untreated control fabric. In contrast, all of the commercial shirts had a negative yellowness index, indicating that they had been treated with a formulation containing bluing. There are significant differences between the initial properties of the several shirts listed in Table XIV, the greatest being those shown by Shirt D. This product had a high crease recovery but low breaking and tearing strengths, indicating that it had received a more severe treatment than the other shirts listed. The fabrics were similar, but not identical, so that some of the differences must be attributed to differences in construction.

Table XV shows the effect of repeated launderings

TABLE XVI. Physical Properties of Shirts After Laundering and Service

Properties of the shirts were measured after they became unwearable or after 50 wearing and laundering cycles.

Treatment	Number of laundering cycles	Yellowness index	Crease recovery, %		Breaking strength, lb.		Tearing strength, g.	
			Warp	Filling	Warp	Filling	Warp	Filling
Laundered commercially								
Epoxide IV	41*	0.04	61	57	36	20	440	334
Epoxide IV	44*	.06	62	62	31	19	480	392
Commercial Shirt A	40*	.01	41	48	23	20	408	390
Commercial Shirt C	20*	.04	42	46	26	24	501	428
Commercial Shirt D	20*	.05	47	59	47	23	478	586
Home washed and tumble dried								
Epoxide IV	50†	.06	64	62	43	21	742	479
Epoxide IV	50†	.05	68	64	39	24	682	470
Commercial Shirt A	50†	.06	56	53	50	30	638	614
Home washed and line dried								
Epoxide IV	50†	.07	66	62	37	18	516	512
Epoxide IV	50†	.03	63	67	38	18	582	486
Commercial Shirt B	50†	.06	48	46	48	33	900	650

* Shirt unwearable.
† Evaluation stopped.

and service on the wash-and-wear properties of the same shirts. In these experiments, the shirts were subjected to three different types of laundering: commercial laundering in several laundries, home washing followed by tumble drying, and home washing followed by line drying. The last named procedure included drying outdoors in the presence of sunlight. After the stated number of cycles, the remaining wash-and-wear properties were evaluated by two methods: home washing and tumble drying, and home washing followed by drip drying on a hanger. The results listed in the table show that shirts treated with Epoxide IV had a high level of durability (with respect to wash-and-wear properties) to all three of the types of laundering examined. The commercial shirts showed varying degrees of durability, but were severely affected by repeated commercial laundering. This can be attributed to the effect of the acid sour which has been reported in the literature [7] and to which reference has been made above.

Additional physical properties of the shirts treated with Epoxide IV and their commercial counterparts are presented in Table XVI. These results indicate that the crease recovery after laundering of the shirts treated with Epoxide IV was superior to that of any of the commercial products, but that the latter on the whole showed a slightly higher retention of strength after prolonged service. This result can be attributed to the slow removal of resin (as evidenced by the decreased crease recovery) of the commercial products, with a consequent gain in breaking and tearing strength. No unexpected properties were discovered in the epoxide-treated shirts during either laundering or service, and it can be concluded that the treatment with Epoxide IV provided a satisfactory treatment with a higher order of durability than is available in the usual commercial products now on the market. Admittedly, however, the treatment would be appreciably more expensive than those now in commercial use, so that it might be necessary to depend on blending or other cost-reducing procedures in order to make the process more nearly competitive. The durability to commercial laundering of cotton treated with a variety of blends of Epoxide IV and commercial nitrogenous resins is now being investigated. Results of actual service tests are not yet available, but the laboratory screening procedures described above may be indicative of performance in service.

Conclusions

A broad range of epoxides is available for the finishing of cellulosic fibers, their properties varying so greatly that they are as different from one another as they are from the commercially available resins. One of the best products examined to date is vinylcyclohexene dioxide. This product performs well in the treatment of cotton, alone and in blends, with most commercially used nitrogenous resins. It is water soluble, resistant to color formation on heating (and in fact appears to protect cotton to a slight degree in this respect), and produces a given level of crease recovery with a somewhat lower loss in strength after treatment than do other epoxides examined. It is not chlorine-retentive, and the treatment is resistant to acid hydrolysis. However, at the present state of knowledge it requires a higher add-on to produce a given improvement in properties than do the commercial nitrogenous resins. It remains to be seen whether this can be overcome by technical improvements, or whether it is inherent in this and other epoxides. The use of suitably chosen blends may remedy this deficiency in part.

To maintain perspective, it is only reasonable to state that there is room for improvement in the properties of all the experimental and commercial shirts or other treated materials examined to date in this laboratory. Even the best treatments available, including those examined here, produce a rather considerable and inherently undesirable loss in strength, although the end-use item is still sufficiently strong to provide good service. None of the shirts examined attained a "perfect" level of wash-and-wear properties, so that it would perhaps be more appropriate to describe them by the term now used by the British: "self-smoothing" fabrics. Perhaps the looked-for improvements will be found in improved catalysis, or in unconventional conditions of application. Work on this field of study and on the examination of other chemical structures continues.

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Performance Characteristics of Chemically Stabilized Cotton Knit Goods[1]

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IN RECENT years there has been a considerable increase in the manufacture and use of cotton knit fabrics.

There are certain classifications of clothing in which knit cottons have always been the dominant fabric; for example, undershirts, union suits, and T-shirts. Other new styles into which knit cottons will automatically expand and hold at least some portion of the market include leotards, the backing for high pile "fur" fabrics, and knitted crib sheets.

Today's increasing consumption of cotton knit fabrics is partly caused by our expanding national market and partly caused by the new styles just mentioned, but it is not entirely attributable to those two factors. Cotton knit fabrics are now able to command markets of which they previously held only a small percentage. Table I indicates that knit cotton fabrics are finding, in other garment fields, an increasing acceptance [2]. For example, knit dresses, of which only 7% were made of cotton in 1955, now are of cotton to the extent of 35% of that market. Even though the knit dress market is a relatively small one, this is an example of the third cause for the expanding consumption of cotton knits. In knitted nightwear, cotton garments have more than doubled their percentage of the market since 1950.

These increases in cotton knit goods production and usage and the accompanying expansion into new fields have been concurrent with the widespread acceptance of the practice of chemically stabilizing cotton knit goods. The latter may be partly responsible for such gains as have been made in knit dresses and knitted nightwear.

There is a question as to why the cotton knit goods market has expended so noticeably. Styles alone cannot be responsible for it.

The performance characteristics which are important in purchasers' minds must certainly be related to the factors which have led to this growth. They may even be the factors themselves.

A recent issue of a popular consumer's magazine [1] carrys an article on a survey of several brands of polo shirts for children. This article indicates that the purchasing public considers three factors to be important in the purchasing of knit goods. In the order of importance they are dimensional control, appearance, and wearing qualities. All three of these are factors which the textile processors modify when they treat with chemical stabilizers.

The purpose of this investigation is to find out what happens to the functionality of the fabric when cotton knit goods are treated with chemical stabilizers. In order to do this it was necessary to first work out methods of laboratory treatment which would yield reproducible results.

The following method was adopted. Samples were cut with a 25-in. length (wale direction) and a 22-in. width. Each sample was then placed on a smooth flat surface and marked with an indelible parallelogram which exactly followed the courses and wales of the fabric. The distances marked along the wales were 15½ in. and those along the courses were 17 in. The fabrics were then wet treated, squeezed through

[1] Presented at the Chemical Finishing Conference of the National Cotton Council of America, Washington, D. C., October 7, 1959.

rollers, and stretched on a frame which had a row of pins forming an 18 × 18-in. square. The marked lines were pierced by the pins in framing the fabric. Each sample was then course and wale counted while on the frame to be certain that the number of courses and wales per inch corresponded to those of all other treated samples. The frame samples were then dried and cured as desired. They were then removed from the frames and evaluated.

The fabric used in this evaluation was handled in the laboratory so that a water blank exhibited exactly 20% wale-direction shrinkage in each application. This mechanical handling left the fabric reasonably relaxed during drying and curing. The 20% length shrinkage on untreated fabric is similar to what might result in a finishing mill if such knit cotton fabric were treated without a chemical stabilizer and without being passed through a tensionless calender.

The course shrinkages were also evaluated in this study, but for the purpose of simplicity all evaluations have been reported with regard to length shrinkage only. The length shrinkage data present the shrinkage control picture just as clearly as do total (wale plus course) shrinkages.

Examinations of the effects produced by chemical stabilizers were carried out with equal solids applications of the five principal types of stabilizing chemicals in use on cotton knits today. These types will be referred to as triazone, triazine, urea formaldehyde, DMEU, and acetal. The solids applications were made at 1, 3, 5, 8, and 12%. This covers a range of applications from too little to too much.

The knit fabric used was a plain knit bleached cotton T-shirt fabric.

For purposes of comparison, 80 × 80 cotton sheeting was treated and evaluated in a parallel series in which the five stabilizing agents were applied to the woven goods in solids concentrations equal to those applied to knit goods.

TABLE I. Use of Knit Cotton Garments

Year	1950	1955	1956	1957	1958
	Knit dresses				
Thousands of bales	0.16	0.5	0.8	1.7	3.5
Cotton percent of total market	5	7	10	15	35
	Nightwear, knit				
Thousands of bales	2.9	6.6		7.9	8.5
Cotton percent of total market	6	12		14	16

Dimensional Control

Dimensional control is the property uppermost in the minds of most finishers when they apply chemical stabilizers. It is generally considered by finishers to be the most important evaluation of the efficiency of a chemical stabilization treatment. In the article on children's polo shirts, dimensional control was also listed as number one among the factors of importance to purchasers of knit goods.

In Figure 1, the percent length shrinkage is plotted against the percent chemical stabilizer for each of the chemicals used. The point-to-point plots for the various concentrations of all the stabilizers are within the outlined area which falls from an initial shrinkage of 20% to less than half of that in the center of the vertical section labelled optimum processing zone.

As a broad generalization it may be said that proper treatment with chemical stabilizers eliminates about half of the inherent shrinkage of a knit fabric. This generalization has been observed many times to be true in mill practice too. Here it can be seen

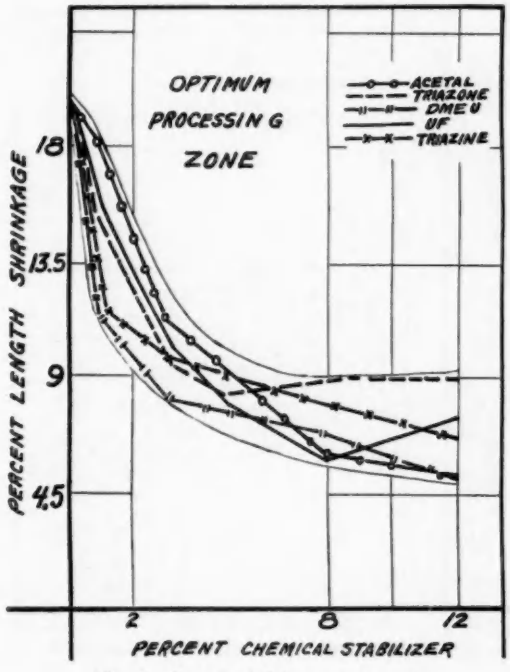

Fig. 1. Length shrinkage; one wash.

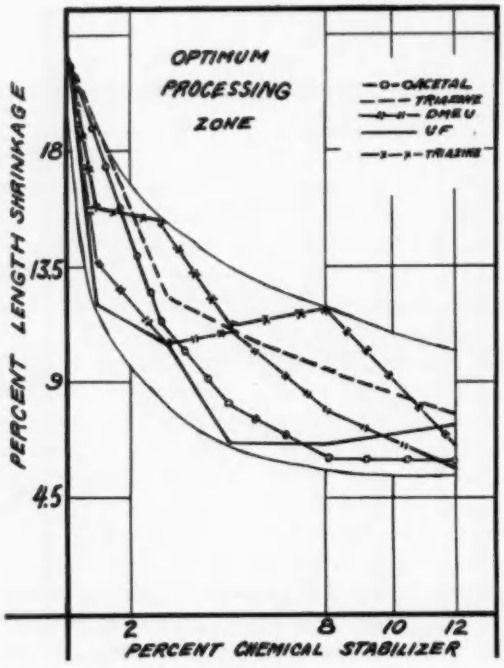

Fig. 2. Length shrinkage; five washes.

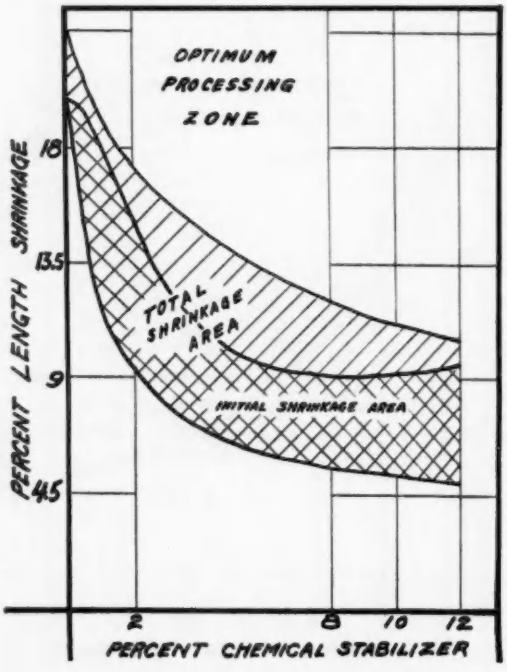

Fig. 3. Length shrinkages; initial and total.

that the full shrinkage of 20% has been reduced to below 10% by all five types of chemical treatment.

The optimum processing zone shown here represents the limits of practical effectiveness in chemical treatment. These limits have been established by taking into account all of the factors studied in this work. Shrinkage control, wash-wear ratings, abrasion resistance, strength loss, and fabric surface appearance are all at their most satisfactory levels within this optimum processing zone. In general the limits are represented by a 2% minimum and an 8% maximum. Economically, 5% is probably the maximum. It can easily be seen from Figure 1 that to treat in the range below 2% will lead to widely variable shrinkage control results. Many of the finishing mills are applying chemicals within the optimum processing zone, but there are some who, for economic reasons, are trying to get by below the minimum. Many customer complaints of unsatisfactory shrinkage control can be traced to applications in the region below 2%.

After five washings with tumble drying, fabrics shrink as shown in Figure 2. An untreated fabric has shrunk 23% at the end of the five launderings. Although the benefits of some of these chemical treatments have been slightly reduced by the washing and

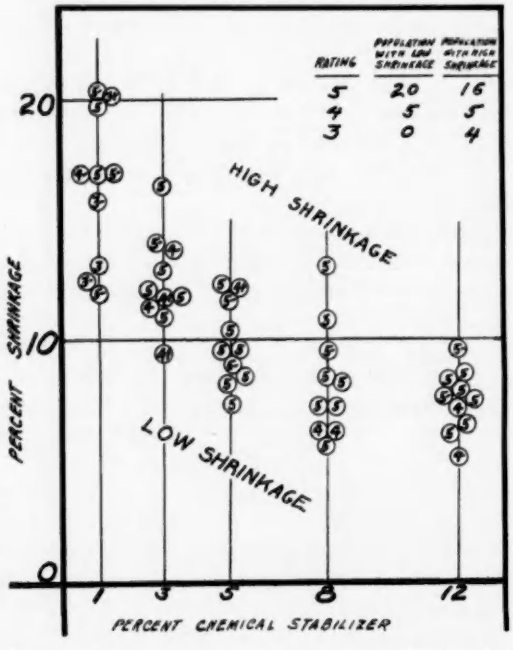

Fig. 4. Wash-wear and dimensional control on knit goods.

some have remained unchanged, it may still be seen in Figure 3, an overlap of Figures 1 and 2, that approximately half of the inherent shrinkage of the fabric has been eliminated by the chemical treatment. From this it may also be said that the improvement in dimensional control is durable to washing.

Appearance

The most pronounced change to be brought about by the applications of chemical stabilizers to cotton knit goods is the improvement in wash-wear ratings when examined according to the Monsanto standards. Table II lists wash-wear ratings for knit fabrics and for woven fabrics treated with the five types of chemicals. The one-wash values are in the upper blocks and the five-wash values are in the lower blocks. The water blanks for knit goods, in the column for 0% on fabric, were rated "2 −" at the first laundering and "1 +" after five launderings. The fact that these fabrics immediately jumped to much higher ratings upon application of small quantities of chemical stabilizers can be seen in the columns for 1% applications. Here even the quantities below the optimum processing zone produced big improvements in wash-wear rating. Most of the ratings at the 3% and 5% application levels are "5" and stay that way through multiple launderings. The over-all enhancement in the wash-wear appearance of knit goods is a durable one. At the "5" wash level the DMEU treated fabric has dropped slightly in rating, but the others have held very satisfactorily.

By comparison of these ratings on knit goods to the corresponding ratings of the identical treatments on 80 × 80 cotton sheeting, it may be seen that good wash-wear ratings are much more easily obtained on knit goods than on woven goods. Note that at 3% and 5% applications on woven goods most of the ratings are only "3" or "4." A "5" rating is rather difficult to obtain on woven goods but, as we have seen here, it can be obtained quite easily on knit goods. Here the chemical stabilizers have made a large and relatively unsung contribution to the improved saleability of cotton knit goods. Maybe this is one of the reasons that cotton knit dresses, cited in Table I, have commanded an increasing portion of that market.

It seems quite reasonable to assume that there might be some correlation between the wash-wear ratings and the dimensional controls produced on knit goods. Figure 4 is a population chart. Here the percent fabric shrinkage obtained at each individual application is marked by a circle containing the wash-wear rating obtained on that sample of fabric. The entire shrinkage area is divided into high shrinkage (10–20%) and low shrinkage (0–10%) portions leaving equal populations of points in the upper and lower halves. The table in the upper right corner summarizes the populations of the individual ratings in each half of the chart.

Of the 25 treatments which produced low shrinkage 20 of them yielded "5" ratings. Note that there

TABLE II. Wash-Wear Ratings

Type of product	Percent on knit fabric				Percent on woven fabric					
	0	1	3	5	0	1	3	5	8	12
One wash										
UF	2−	3−	4	5	2	2−	3+	4+	5	5
Triazone	2−	4+	4−	5	2	3	3	4+	4+	5
DMEU	2−	5−	5	5	2	2	4−	5	5	5
Acetal	2−	5−	5	5	2	3−	3	3	3	3
Triazine	2−	5−	5	5	2	2	3+	4−	4+	5−
Five washes										
UF	1+	3−	5	4+	1	3−	3	4−	5−	5
Triazone	1+	3+	4−	5−	1	2	3+	5−	5	5
DMEU	1+	3	4+	5	1	2	4−	4	4	5−
Acetal	1+	5	5	5	1	3−	3	3	3	3
Triazine	1+	5	5	5	1	1	3	3	4+	5

Optimum processing zone

are no "3"-rating treatments in the low shrinkage area.

In the high shrinkage half there are only 16 "5" ratings. There are 5 "4" ratings and 4 "3" ratings.

From the upper half of this chart and the column on the right it may be seen that good wash-wear ratings can be obtained without being accompanied by good shrinkage control.

From the lower half of the chart and the middle column it may also be concluded that good shrinkage control will nearly always be accompanied by good wash-wear ratings.

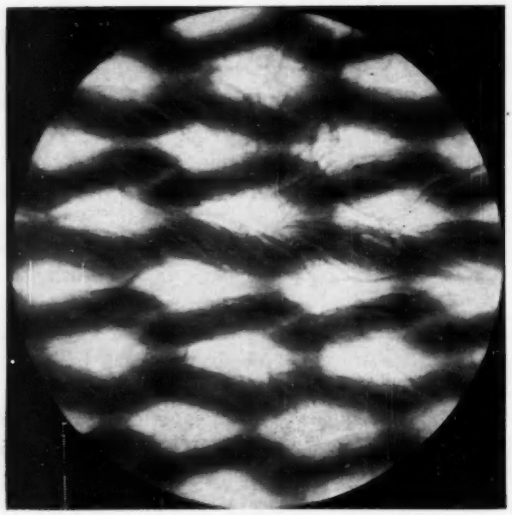

Fig. 5. Magnification 16.6 ×.

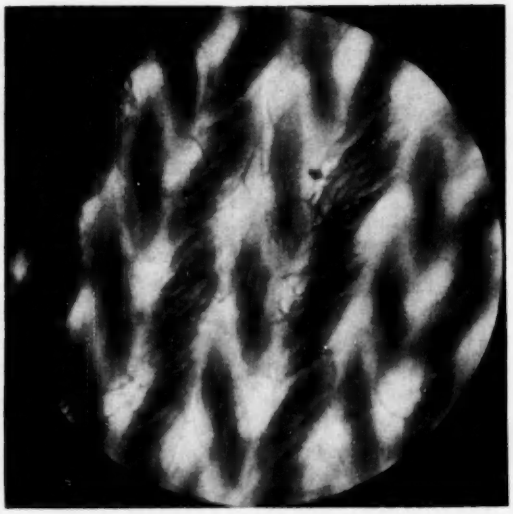

Fig. 5A. Magnification 16.6 ×.

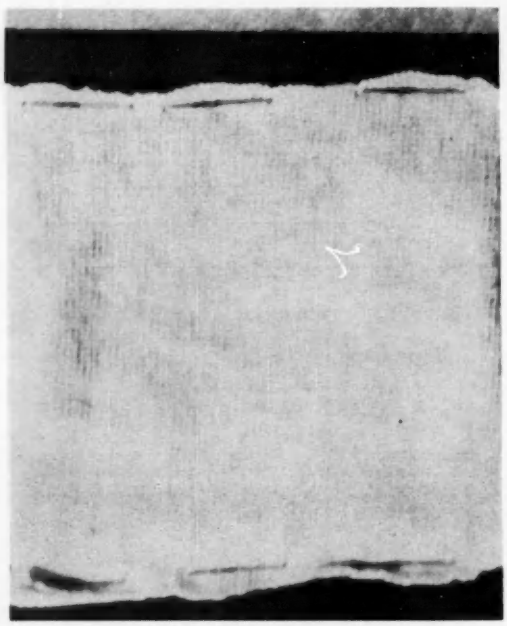

Fig. 6.

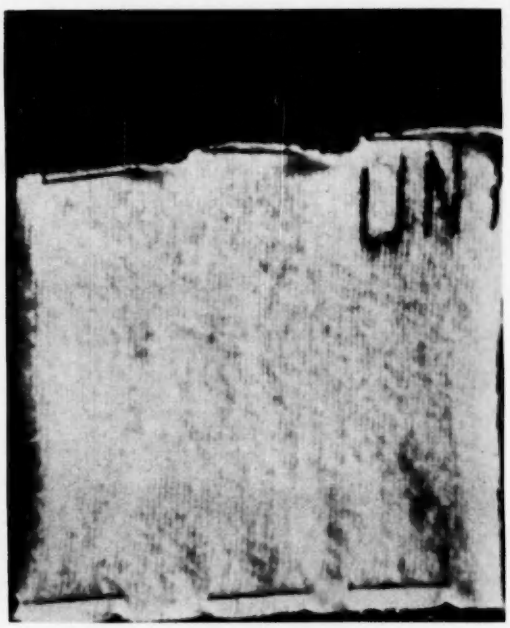

Fig. 6A.

Surface Appearance

Laundering and tumble drying treated and untreated fabrics produces observable differences in surface appearance.

Figure 5 is a close-up of a treated fabric after five launderings. Figure 5A presents an untreated fabric at the same magnification after five launderings. In the untreated fabric the yarns have lost their tight structural unity. They have tended toward becoming loose masses of fibers rather than tightly wound units as they originally were.

In Figure 6 the surface of a treated fabric after five launderings may be seen to be smooth and relatively free of pilliness and fuzziness. In Figure 6A the corresponding untreated fabric displays a very poor surface appearance after five launderings.

The above improvements in smooth drying properties, wash-wear ratings, and surface appearance have been beneficial to cotton goods treated with chemical stabilizers. These chemically produced advantages may not be obvious to the consumers, but they certainly must have added to the satisfaction in the use of cotton knit goods.

Crease Resistance

In the evaluation of woven goods, crease resistance and wash-wear ratings are generally thought to be closely related. Although crease resistance cannot be used as a direct measurement of wash-wear qualities on woven goods, it does give a good indication of what is to be expected. On either woven goods or knit goods, good crease resistance values indicate good appearance during wearing.

To our knowledge the measurement of crease resistance on knit goods has not previously been reported. There was even doubt that it could be done with any degree of reliability. Figure 7 presents a structural picture of a piece of knit goods such as was used in this study. Attempts to evaluate the crease resistance were made by cutting the Monsanto tester samples so that the fold would fall (1) along the courses, (2) diagonally, or (3) along the wales.

Consistently reproducible results were obtained in the measurements made with the fold parallel to the wales.

It can be seen in Figure 7 that if the fold were made parallel to the courses, as at Point A, the yarns

TABLE III. Crease Recovery Increases

	Percent chemical stabilizer	Acetal		Triazine		DMEU		UF		Triazone	
		K	W	K	W	K	W	K	W	K	W
Water blank	0	106	70	106	70	106	70	106	70	106	70
Crease angles before laundering	1	130	101	125	96	122	101	127	100	130	96
	3	137	97	142	113	128	110	139	116	131	109
	5	154	96	140	117	141	124	146	129	135	126
	8	148	94	147	130	156	140	153	144	138	130
Crease angles after five launderings	1	129	101	120	106	120	112	117	101	103	93
	3	136	100	121	119	125	121	123	113	113	109
	5	154	99	140	126	134	129	132	121	128	103
	8	152	96	122	140	126	148	135	131	136	126
Initial crease angle increase	1	24	31	19	26	16	31	21	30	24	26
	3	31	27	36	43	22	40	33	46	25	39
	5	48	26	34	47	35	54	40	59	29	56
	8	42	24	41	60	50	70	47	74	32	60
Residual crease angle increase	1	23	31	14	36	14	42	11	31	−3	23
	3	30	30	15	49	19	51	17	43	7	39
	5	48	29	34	56	28	59	26	51	22	33
	8	46	26	16	70	20	78	29	61	30	56
Effect of laundering	1	−1	0	−5	+10	−2	+11	−10	+1	−27	−3
	3	−1	+3	−21	+6	+3	+11	−16	−3	−18	0
	5	0	+3	0	+9	−7	+5	−14	−8	−7	−23
	8	+4	+2	−25	+10	−30	+8	−18	−13	−2	−4

K = knit goods; W = woven goods.

might merely act as a hinge and thus prevent any measurement of the resilience produced by chemical treatment. When folds were made diagonally, as indicated by Point B, variable results were obtained because it was not possible to consistently cut the samples so that the fold would fall along the same

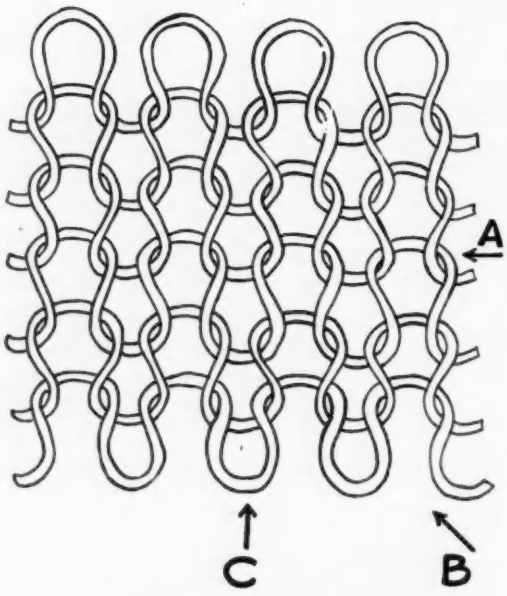

Fig. 7. Creasing of knit goods.

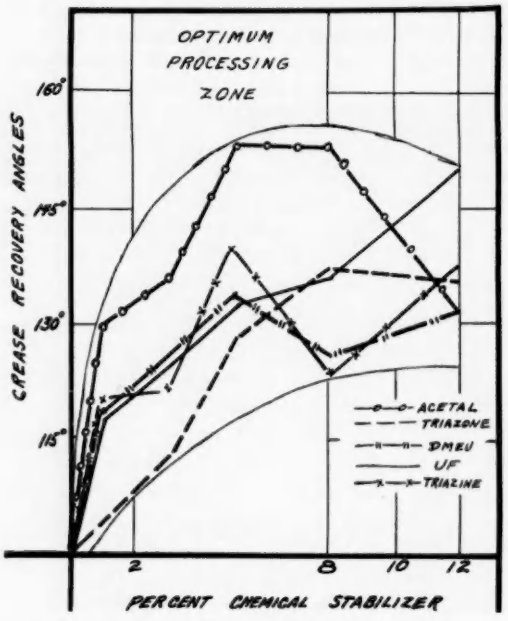

Fig. 9. Crease recovery angles; five washes.

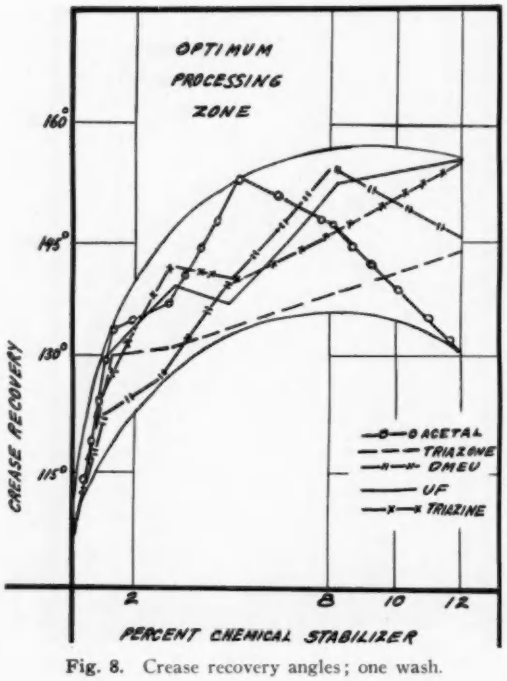

Fig. 8. Crease recovery angles; one wash.

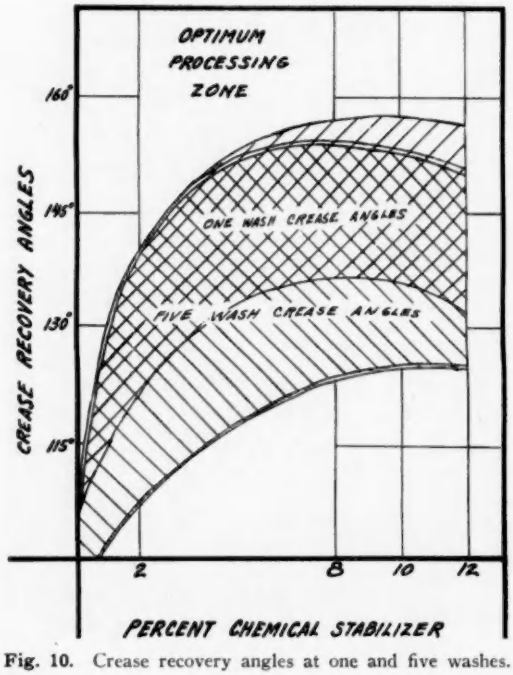

Fig. 10. Crease recovery angles at one and five washes.

diagonal each time. Samples folded parallel to the wales, along Line C, gave reproducible results. Close examination of samples which had been folded for testing along the wales showed that the fold always came at Point C and not at the juncture of two yarns to the right or left of that point. The results obtained by this procedure were not only reproducible for any one sample but they also gave the expected wide differences between treated and untreated samples. Likewise, the treated sample results, with one exception, corresponded with those expected from the known properties of the treating chemicals.

Figure 8 demonstrates the general order of crease resistance to be expected from the applications of the five types of chemical stabilizers. Figure 9 shows the same after five launderings. Here the general crease resistance area has been broadened by virtue of the fact that four of the products have washed down from their initial crease recovery values. Figure 10 presents an overlap of the general areas of crease recoveries to be expected at the one-wash and five-wash levels.

An attempt has been made to compare the crease resistances produced on knit goods to the corresponding crease resistances produced on woven goods. To do this the crease recovery increases have been calculated. Crease recovery increases are merely the differences between the values for treated fabric and the values for the corresponding untreated fabric. Woven goods crease recoveries were taken only in the warp direction (Table III).

Plotting of the crease recovery increases for both woven goods and knit goods against the applied concentrations of the chemical stabilizers yields some sur-

TABLE IV. Dimensional Control Improvement per Unit Strength Loss

	Percent stabilizer	Acetal	Triazine	DMEU	UF	Triazone
One wash	1	0.7	1.8	0.7	1.0	0.9
	3	4.5	1.3	1.0	1.2	1.3
	5	2.3	1.4	1.0	1.2	1.0
	8	1.7	1.2	1.2	1.1	1.0
	12	2.7	1.3	1.0	1.7	1.0
Five washes	1	0.6	1.0	0.9	0.8	0.3
	3	2.6	0.7	1.0	1.1	0.9
	5	3.0	1.0	1.2	0.8	0.9
	8	1.8	1.0	1.2	1.0	1.0
	12	2.1	1.3	1.0	1.1	1.1

$$DCI/TL = \frac{\text{Percent of total shrinkage eliminated}}{\text{Percent reduction of strength}}.$$

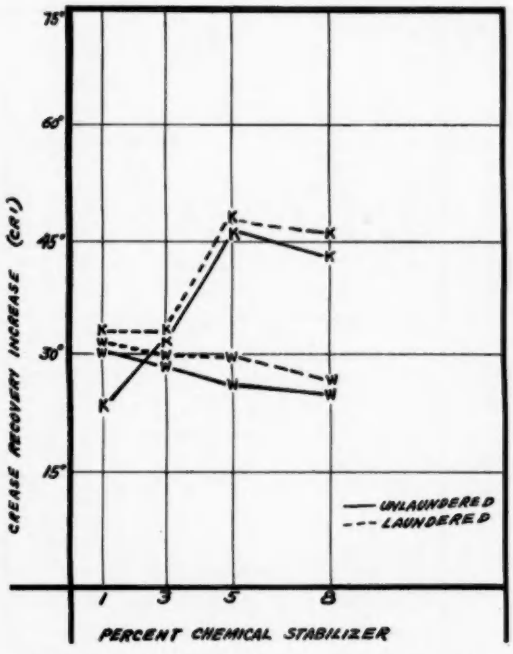

Fig. 11. CRI with acetal; woven and knit goods.

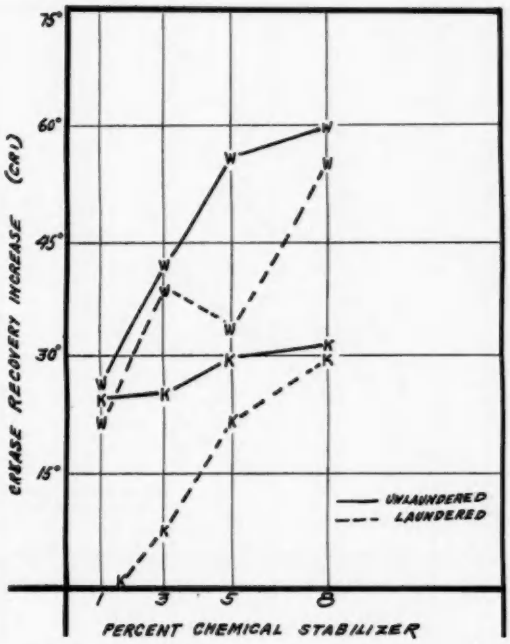

Fig. 12. CRI with triazone; woven and knit goods.

prisingly parallel effects. An exception is the acetal shown in Figure 11, which is one designed specifically for strength preserving and dimensional control of knit goods and is not intended for application to woven goods. Here the solid lines represent the unlaundered values for the same fabrics. The K lines are knit goods values and the W lines are woven goods plots. Here it can be seen that increasing quantities of the acetal produce increases in crease recovery on knit goods but do not do so on woven goods. The crease recovery value remains steady about 30° above the untreated value on the woven goods and climbs to about 45° above the untreated value on knit goods.

The triazone (Figure 12) produces ascending CRI values with increasing applications on woven goods but holds at approximately 30° increase across the board on knit goods. The crease resistance benefits of the lower applications of the triazone on knit goods are removed by washing.

The triazine (Figure 13) also produces ascending CRI values on both fabrics; it shows a laundry loss on knit goods only at the very high concentration. In Figure 14 the DMEU acts similarly.

The UF (Figure 15) displays ascending CRI values and comparable wash-downs for both knit goods and woven goods.

Figure 16 is a population chart relating wash-wear appearance to crease recovery. Here the crease recovery obtained by each individual application is plotted as a circle containing the wash-wear rating obtained on that sample of fabric. The entire area is divided into high and low crease recovery halves. The populations of the ratings are summed up in the table at the top. In the high crease recovery half 22 of 25 treatments have produced "5" ratings. The remaining 3 are "4 +" ratings. In the low crease recovery half there are 4 "3" ratings, 7 "4" ratings, and only 14 "5" ratings. This indicates that low crease resistances do not always yield low wash-wear ratings. Some of the lowest crease recoveries have been accompanied by good wash-wear ratings. However, the lower half of the chart, representing good crease resistance values, indicates that high crease resistance will always yield good wash-wear ratings.

Wearing Qualities

The foregoing has presented the advantages of improved dimensional control and improved wash-wear appearances which have resulted from the treatment

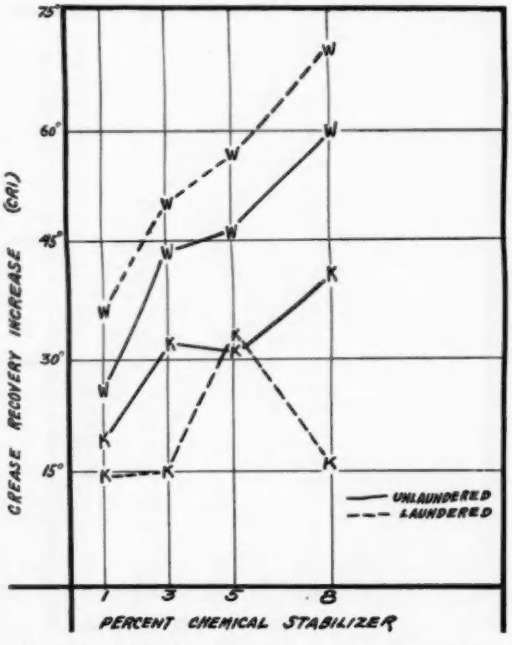

Fig. 13. CRI with triazine; woven and knit goods.

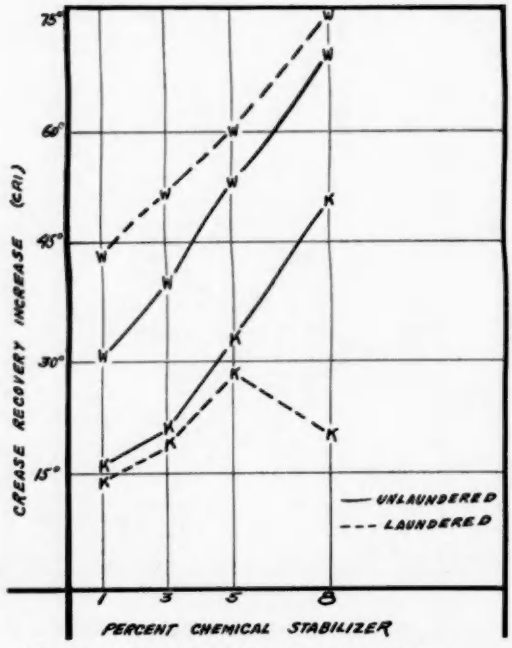

Fig. 14. CRI with DMEU; woven and knit goods.

of cotton knit goods with chemical stabilizers. The accompanying disadvantages must also be considered. These are strength loss and loss of abrasion resistance.

Figure 17 presents the original strengths in pounds of the treated fabrics at the various applied concentrations of individual chemical stabilizing agents. Figure 18 presents the same values after five launderings. It can be seen that there are fairly wide differences of strength loss within the optimum processing range for the various chemical types. It can also be seen that the washing of all fabrics effects a slight restoration of the lost strength but certainly never returns the fabric to its original bursting strength of 62 lb.

Strength loss may be considered to be the price paid for the advantages gained in dimensional control and wash-wear appearance. If the percent of inherent shrinkage removed is considered to be the benefit gained, and the destroyed portion of the total strength of the fabric is considered to be the price paid therefor, a simple efficiency factor of percent dimensional control improvement per unit strength loss may be calculated (Table IV). Plots of these efficiency factors at the five-wash levels are given in Figure 19. Most of the chemical products function with about the same degree of efficiency.

Abrasion Losses

Abrasion losses of the knit goods were evaluated by abrading the samples in the AATCC Accelorotor. Quintuplicate samples were individually abraded 2 min. at 3000 r.p.m. They were weighed before and after abrasion treatment. In Figure 20 the percent weight losses are plotted against the concentrations applied. An untreated sample lost 2.4% of its weight. It must be noted that these fabrics were treated with no softener in the bath. The presence of softeners may help to minimize the heavy weight losses which have occurred with some of the chemical stabilizers.

The photograph in Figure 21 shows samples which were treated at the 3, 5, and 8% levels and later abraded in this test. In certain of these treatments the samples have worn so thin that the dark background can easily be seen through them; yet they have not developed holes. Note this in the 5% UF and triazone treatments and in the treatments with 8% triazine, UF, and triazone. These samples all showed at least 20% weight loss in the course of the abrasion testing. It is interesting to note, also, that the fabrics treated with the 8% level of UF and

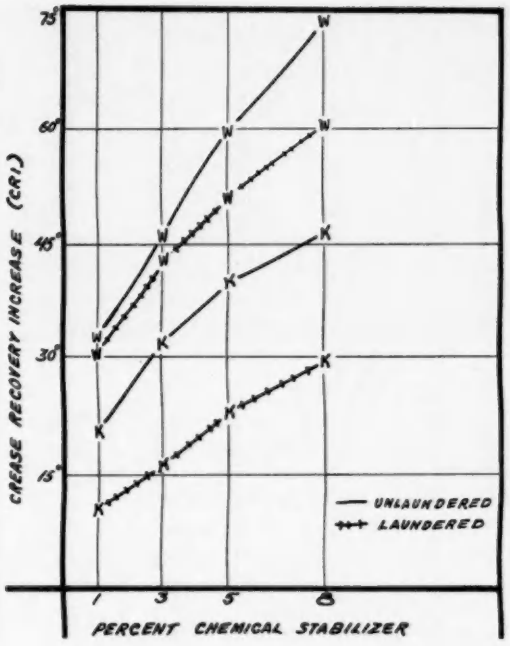

Fig. 15. CRI with UF; woven and knit goods.

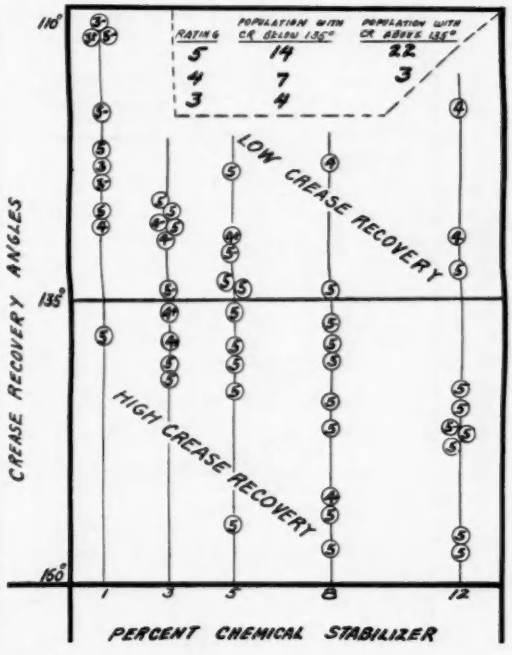

Fig. 16. Crease recovery vs. wash-wear ratings.

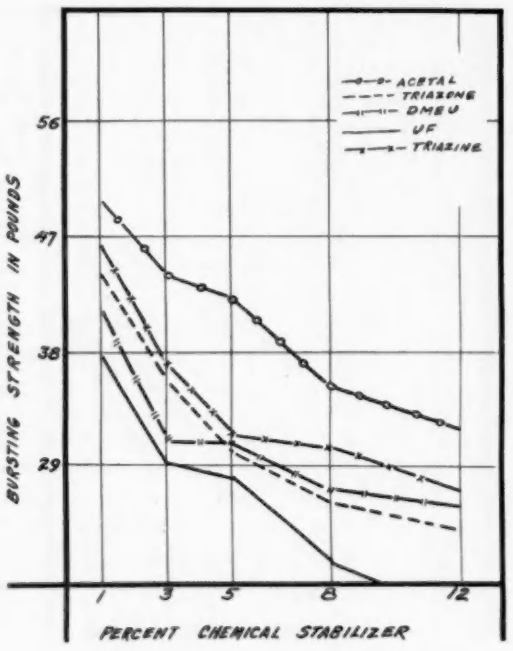

Fig. 17. Bursting strength; original.

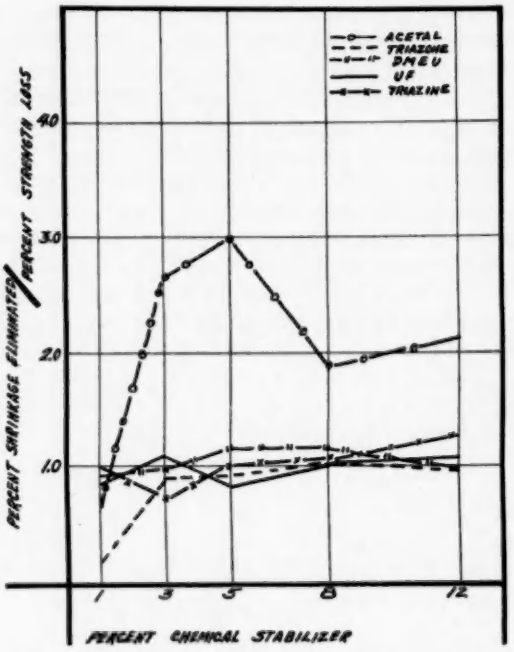

Fig. 19. Dimensional control improvement per unit strength loss.

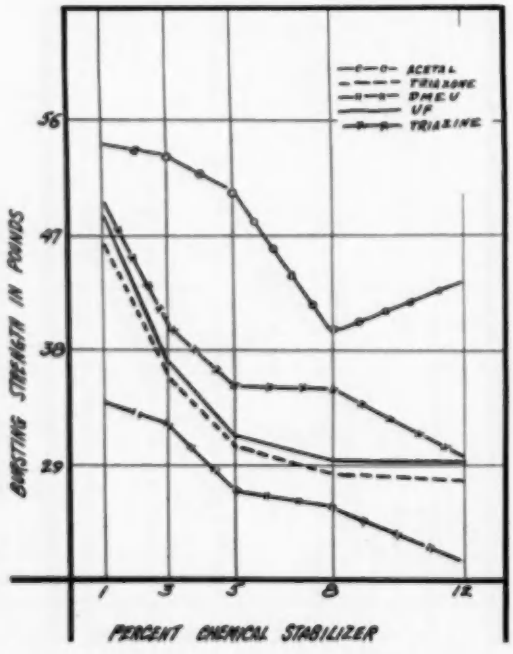

Fig. 18. Bursting strength after five launderings.

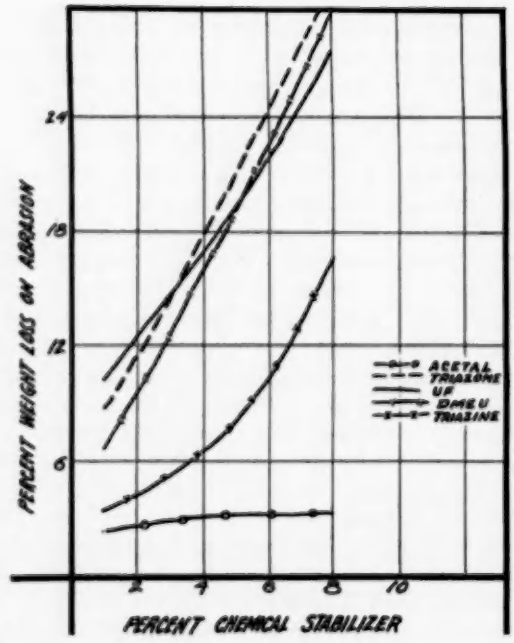

Fig. 20. Abrasion resistance.

triazone, which have lost even more weight (approximately 30%), have not developed holes. This is an indication of the excellent wearing qualities of the knit goods structure.

Summary

Chemical stabilizers have been shown to impart four advantages to cotton knit fabrics. They reduce the shrinkage by half, make a pronounced improvement in the wash-wear appearance of the fabric, preserve the surface appearance of the knit goods through laundering, and impart crease resistance which helps to maintain a better appearance during wearing.

The accompanying losses of bursting strength and abrasion resistance have a minimum effect on the use properties of the fabric because of the flexibility of the knit structure.

It appears that the chemical stabilizers do as much (or more) to enhance the good properties of knit goods as do the crease resistant materials for woven goods. They not only produce enhancing effects on the performance of knit goods, but at the same time they are able to do it when applied in low quantities and with a minimum of damage from loss of good properties. The effects produced appear to be durable for the life of the fabric. It may be concluded that the chemical stabilization process will continue to contribute to the saleability of cotton knit goods.

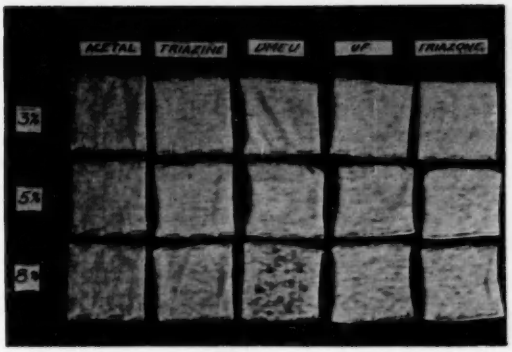

Fig. 21.

Acknowledgments

The fourteen thousand determinations carried out in preparing this paper were very ably done by Mr. A. R. Clawson. Photographs used in this paper were prepared by C. J. Bunczk, M.R.P.S.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

The Effect of Fiber Parameters on the Wash-and-Wear Characteristics of Wool Fabrics

Harris Research Laboratories, Inc.
6220 Kansas Avenue, N. E.
Washington 11, D. C.
November 6, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The effect of fiber parameters on the fulling propensity and felting shrinkage in laundering of wool materials has been studied extensively, with somewhat inconsistent results [1, 4, 7, 10, 11, 12, 14]. The object of the present work was to study the effect of fiber parameters not only on shrinkage but also on the other wash-and-wear characteristics, such as mussing and fuzzing, of wool fabrics which have been laundered in modern home washing machines and tumble dryers. Washing in these machines, which have much gentler mechanical action than earlier tumble washers, was found to produce little or no shrinkage and good wash-and-wear appearance with several commercial wool fabrics previously studied [2, 3, 5, 6].

Three sets of fabrics were used for this work.[1]

1. Five heavy wool serge uniform fabrics varying in wool grade, in viscose content, and in the denier of the viscose fiber (Table I).

[1] The authors are indebted to the Textile Research Institute, Princeton, N. J., and to Dr. S. J. Kennedy, Textile Clothing and Footwear Division, Quartermaster Research and Development Center, Natick, Mass., for these special fabrics.

TABLE I. The Effect of Fiber Parameters on Shrinkage, Mussiness, and Fuzziness of Experimental Uniform Fabrics *

Fiber content					
Wool: Grade	60's	56's	60's	56's	56's
%	100	100	70	70	70
Viscose: Denier	—	—	3	3	5.5
%	—	—	30	30	30
Area shrinkage, %					
10 Laundering and tumble drying cycles	5	4	5	3	3
Mussiness rating					
1 Laundering and tumble drying cycle	4.3	4.8	5.1	5.6	5.2
5 Laundering and tumble drying cycles	4.8	4.8	5.2	5.4	5.2
10 Laundering and tumble drying cycles	4.6	5.4	3.5	3.6	3.9
Fuzz formation in laundering					
10 Laundering and tumble drying cycles	0.9	1.0	1.0	1.0	0.8

* Fabric specifications: yarn, 2/25 worsted count; texture, 68 × 54; weave, 2/2 twill; weight, approx. 12 oz./yd.[2]

2. Six worsted, lightweight fabrics, each available in the off-the-loom, ready-to-dye, and dyed states, and differing only in fiber length, diameter, and crimp ([13] and Table II).

3. Two woolen, lightweight fabrics, differing only in crimp, in the ready-to-dye state and dyed in three colors ([8, 9] and Table III).

The methods used for determining relaxation and laundering shrinkage and for subjective ratings of mussiness and fuzz formation in laundering have been described elsewhere [2, 5, 6].

The data in Table I show that heavy fabrics made from coarser wools, alone and in blends, exhibited slightly less laundering shrinkage than those incorporating finer wool fibers. The denier of the viscose had no effect. A similar effect of wool fineness is shown in Table II; the fabrics containing Wool B (high diameter, short staple, high crimp) shrank consistently less than the others. Next in order was Wool D (high diameter, long staple, low crimp), and, at a higher shrinkage level, Wool S (high diameter, low length, high crimp). The differences among the other wools, all somewhat finer but varying in length and crimp, appeared insignificant. As re-

TABLE II. The Effect of Fiber Parameters on the Shrinkage, Mussiness, and Fuzziness of TRI Worsted Fabrics *

Wool designation	D	B	S	O	A	C
Fiber parameters†						
Diameter, μ	23.1	23.2	23.0	21.7	19.9	2.10
Length, in.	2.78	2.14	2.09	2.31	2.48	2.11
Crimps/in.	10.1	15.5	16.4	14.6	10.9	15.9
Area shrinkage, %						
10 Laundering and air drying cycles‡						
Loom state	26	23	23	24	25	26
Ready-to-dye	5	3	6	6	7	6
Dyed	3	1	3	5	5	4
10 Laundering and tumble drying cycles						
Loom state	34	29	33	34	32	30
Ready-to-dye	14	11	20	20	18	20
Dyed	10	9	15	18	18	18

* Fabric specifications: yarn, 1/20 worsted count; texture, loom state: 43 × 39, ready-to-dye: 48 × 42, dyed: 51 × 44; weave, plain; weight (dyed), 6 oz./yd.²

† Data from Textile Research Institute.

‡ After mild machine washing, swatches were flattened and air dried overnight.

TABLE III. The Effect of Fiber Crimp on Shrinkage, Mussiness, and Fuzziness of TRI Woolen Fabrics *

	Ready-to-Dye		Dyed							
			Tan		Blue		Red		Average	
Fiber crimp	High	Low	High	Low	High	Low	High	Low	High	Low
Area shrinkage, %										
10 Laundering cycles										
Air dried	11	14	10	11	11	12	10	11	10	11
Tumble dried	16	20	14	14	16	17	17	16	16	16
Mussiness rating										
Tumble dried	3.7	3.8	3.9	3.9	3.7	3.5	3.4	3.3	3.7	3.6
Fuzz formation in laundering										
Tumble dried	1.0	1.6	1.4	1.6	1.6	1.4	1.5	1.8	1.5	1.6

* Fabric specifications: yarn, 6 run; texture, 42 × 34; weave, plain; weight, approx. 5 oz./yd.²

gards the influence of crimp level, the data of Table III indicate that high crimp fibers tend to reduce laundering shrinkage slightly.

The heavy fabric made from 56's wool was clearly less mussy after laundering and tumble drying, but there was no difference in fuzz formation. While the blends were similar to the all-wool fabrics in mussiness after the early laundering cycles, they grew progressively worse. Progressive increase of mussiness, due to repeated launderings up to 10 cycles, had not been observed in earlier experiments covering a number of commercial wool fabrics which had reasonable resistance to shrinkage due to construction or chemical treatment [5].

The fabrics listed in Table II cockled, and their mussiness and fuzz formation could not be compared. The fabrics listed in Table III, made with fibers of different crimp levels, showed no consistent difference with regard to these characteristics.

There are fewer coarser than finer fibers in a given yarn weight, and each coarse fiber requires more work for bending and movement. These factors could easily lead to less fiber entanglement and lower shrinkage. Similarly, more work is necessary to displace thicker fibers, and this could account for the lower mussiness of the fabrics made from 56's as compared to those made from 60's wool.

The use of coarse fibers seems to be of some minor advantage in wash-and-wear wool fabrics, but it appears likely that the effects of fiber parameters could be masked in the fabrics with the compact constructions needed for wash-and-wear performance of untreated wool fabrics. The effects of construction will be discussed in a future publication; they may explain the rather inconsistent findings reported in the literature on the effect of fiber properties on felting shrinkage.

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HAZEL E. HARRIS

The Hemicelluloses of Roselle Fiber (*Hibiscus sabdariffa*)

Technological Research Laboratories
Indian Central Jute Committee
Regent Park, Calcutta-40
India
October 29, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Roselle fiber, which is used as a substitute for jute, has been shown to be somewhat inferior [2], although the chemical composition [6] of the fiber is similar to that of jute. A detailed study on the structure of the hemicelluloses from roselle fiber has been undertaken, and some preliminary results are reported here.

A sample of roselle fiber on analysis [4] showed alpha-cellulose (59.7%), pentosans (17.6%), uronic anhydride (4.20%), lignin (7.82%), acetyl (4.76%), nitrogen (0.12%), fat and wax (0.58%), and ash (0.47%). The fiber, exhaustively extracted with a mixture of alcohol benzene (1:2, wt./wt.), was cut into small pieces and delignified with sodium chlorite [5]. The holocellulose thus obtained was treated with 10% (wt./vol.) aqueous sodium hydroxide solution for 1.5 hr. at room temperature (30° C.). The mixture was filtered through a sintered glass funnel and the filtrate cooled, then acidified with acetic acid; hemicellulose I was precipitated by the addition of an equal volume of alcohol. Hemicellulose I was filtered and to the filtrate more alcohol (1.5 times) was added to precipitate hemicellulose II. Both hemicelluloses I and II were washed with alcohol, treated with HCl in alcohol (1:10), finally with alcohol alone, and dried in a vacuum desiccator. The yield of hemicelluloses I and II were 16.1% and 0.66% respectively on the oven-dry weight of the fiber. Analyses of hemicelluloses I and II are given in Table I.

On hydrolysis with normal H_2SO_4 on a boiling water bath for 10 hr., both hemicelluloses I and II showed the presence of some acidic components and also some neutral sugars. The main acidic components on chromatography with the solvent system, ethyl acetate–acetic acid–formic acid–water (18:3:1:4), run at the same rate as 4-O-methyl-D-glucuronic acid and 2-O-(4-O-methyl-α-D-glucuronopyranosyl)-D-xylose from jute [1, 7, 9]. Xylose was the main component of the neutral sugars. The hydrolysate from hemicellulose I was treated with Amberlite 1R45 anion exchange resin to remove the acidic components. The resulting syrup yielded crystalline D-xylose which after recrystallization from aqueous ethanol (90%) had m.p. 144° C. and $[\alpha]_D$ + 18° (C, 2.0 in water). The dimethyl acetal of the dibenzylidene-D-xylose [3, 10] had m.p. 210° and $[\alpha]_D^{20}$ − 8.2° (C, 0.49 in chloroform). Besides xylose, other sugars present in the neutral fraction were galactose, glucose, mannose, and rhamnose. The sugars were separated on Whatman filter paper No. I with solvent system butan-1-ol–pyridine–water [10:3:3] and were estimated with Somogyi's copper reagent [8]. The proportion of the sugars, in the order as mentioned above, was 97, 0.35, 1, 0.67, and 1 for hemicellulose I and 65.8, 2.9, 14.4, 12.2, and 4.7 for hemicellulose II.

Acknowledgment

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P. C. DAS GUPTA

TABLE I

	Uronic anhydride, %	Pentosans, %	Methoxy, %	Eq. wt.	$[\alpha]_D^{20}$ (C,1 in *N* NaOH)
Hemicellulose I	16.8	80.8	3.15	1122	−73°
Hemicellulose II	17.1	54.7	3.75	1063	−50.2°

A Miniature Spinning Test for Cotton[1]

Spinning Test Laboratory
The Egyptian Testing House
Alexandria, Egypt
October 24, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

On page 705 of the September 1959 TEXTILE RESEARCH JOURNAL, in a paper by Landstreet, Ewold, and Kerr, mention is made of the possible development of a spinning test economically feasible to test large populations. Such a test is already in operation here, where we are testing 384 samples daily on purely routine work, giving mean strength from 8 lea tests on 8 separate spindles from 4 ring frames, using an 80-g. sample. Merely by completing our existing ring frames, this output can be raised to at least 640 samples per 8 hours or 320 samples processed and spun in duplicate, giving a mean which is from 16 spindles and needs no correction for route variations.

We use modified standard equipment, and our machinery and sequence is as follows:

Four First Cards, making laps for
Four Second Cards, delivering sliver to
Two Balances, producing constant weight for
Eight Drum Lappers, winding constant length bobbins for
First Drawing, 8 deliveries, draft 8, feeding
Second Drawing, 8 deliveries, draft 8, feeding
Third Drawing, 8 deliveries, draft 8, feeding
Slubber, 32 spindles operating, double roving, 2 doffs for
Intermediate, 32 spindles operating, double roving, 2 doffs for
Rover, 64 spindles operating, double roving, 2 doffs for
Four Ring Frames, single-sided, 32 spindles each, producing 60's (9.8 Tex) yarn for
Eight Wrap Reels, motor driven, followed by
Eight Lea Testers, motor driven, followed by
Two Balances for counts determination.

Results are available within 24 hr. if required, and within 48 hr. as routine, from the time at which processing of the sample commences.

FRANK DUNKERLEY

[1] Further information is published in the 16 issues of Explanatory Series A, plus the December 1958 Supplement; a few copies are available to interested persons on request to the address given.

Textile Chemists

Courtaulds (Alabama) Incorporated,

a manufacturer of cellulosic fiber,
has developed a need for a Section Leader,
Textile Chemistry, in the
Utilization Research and Development Department
because of an expanding program in introducing
new cellulosic fiber to textile and related industries.
Candidates must have an M.S. or Ph.D. in
Chemistry or Chemical Engineering, or an M.S.
in Textile Chemistry, with at least five years'
capable experience in the textile chemical
finishing field. Age preferred from 30
to 40 years. This position presents
a challenging and outstanding opportunity
for growth and entails the exercise of
imagination and initiative. Excellent salary
and liberal fringe benefits. Please send
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